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Advances in Analysis and Detection of Explosives

Proceedings of the 4th International Symposium
on Analysis and Detection of Explosives,
September 7-10, 1992, Jerusalem, Israel

Jehuda Yaron (Editor)

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edited by

Jehuda Yinon

*Department of Environmental Sciences
and Energy Research,
Weizmann Institute of Science,
Rehovot, Israel*

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PREFACE

This book represents a collection of papers presented at the 4th International Symposium on Analysis and Detection of Explosives held at the Mitzpeh Rachel Kibbutz Guesthouse in Jerusalem, September 7 to 10, 1992. The Symposium was attended by 150 participants from 20 countries and 50 lectures were given including 4 invited keynote lectures.

The purpose of the Symposium, as the previous Symposia, was to present and to discuss new approaches, new applications, new methods and techniques in analysis and detection of explosives. The Symposium was, according to the feedback received from many participants, very successful and met the anticipated expectations. New collaborative initiatives between various laboratories from different countries were formed, which is a necessity in our common goals of law enforcement, aviation security and environmental quality, issues which are closely related to the analysis of explosives.

I would like to extend my thanks to the Weizmann Institute of Science and the Israel National Police for sponsoring the Symposium, to the contributing Institutions and Agencies for making this Symposium financially possible, and to the members of the International Committee for helpful advice. I am most thankful to my colleagues from the Organizing Committee, especially Dr. Joseph Almog and Dr. Shmuel Zitrin from the Israel National Police, for helping in the organization of this Symposium.

Jehuda Yinon

**4th International Symposium on Analysis and Detection of Explosives
September 7-10, 1992, Jerusalem, Israel**

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BIRMINGHAM SIX PUB BOMBING CASE

A. W. SCAPLEHORN

*Home Office Forensic Science Service
Priory House
Gooch Street North
Birmingham B5 6QQ
England*

ABSTRACT. The forensic science evidence presented at the original trial and in the subsequent Appeals in the Birmingham pub bombing case is described together with the issues identified and lessons learnt that have a bearing on the roles and responsibilities of forensic scientists and how forensic scientific work should be undertaken.

The release in the last few years of a number of individuals including the Maguire family, the Birmingham Six, Judith Ward and the Guildford 4 who were all convicted in the 1970s for terrorist bombings in mainland Britain has been widely publicised.

Each case has had fairly detailed press coverage and such headlines as "Forensic Science at the Cross Roads", "Bias and false claims by Government Forensic Scientists", "Mischief and the Expert Witness", "Criminal Injustice" and so on have all brought the role and responsibility of forensic scientists into sharp focus. In the course of this presentation I want to deal with one of those cases, that of the Birmingham Six convicted for two horrendous pub bombings in 1974, to outline to you what occurred and more importantly, the lessons we as representatives of the forensic community might learn from it and how we should be moving forward with perhaps some form of international agreement for the technical standards to be used and the roles of forensic scientists and further co-operation in such cases. The case identified many issues and work is ongoing. Clearly international meetings such as this one are a manifestation of our willingness to share experiences and to move forward and the organisers are to be congratulated for arranging such a detailed, stimulating and interesting programme.

Lying off the west coast of Britain is Ireland. It is very green and attractive country, the scenery is remarkable, climate agreeable and the people very friendly. However, over the years it has had a very chequered history. In 1922 the predominantly catholic South became self governing state with Dublin as the capital but the more protestant North remained part of the United Kingdom.

Lack of opportunities amongst the significant catholic community in the North led to agitation in the sixties for unification and there was not only a strong political force for this but it was augmented by pressure from paramilitary terrorist groups such as the IRA and PIRA and to counter these equivalent organisations were formed on the loyalist side. The British Government response was to send troops to maintain the peace and a number of political initiatives were mounted, however indiscriminate sectarian killings and bombings of military and commercial targets became the order of the day and continue to this time, there were several

killings last week and bombs exploded at the London Hilton hotel yesterday.

In January 1972, 13 Catholics were shot in Londonderry by British soldiers and in addition to heightened violence in the Province the following month saw the bombing campaign spread to mainland Britain with a large bomb outside the Parachute Regiment in the Army town of Aldershot which killed 7 people.

The campaign started in the Midlands of England in Birmingham in August 1972 and thereafter incidents occurred in waves and there were about 50 bomb incidents of various sizes in the period leading up to the pub bombings in late 1974.

Birmingham is the second largest city in England, some 120 miles from London. It is a vibrant industrial, commercial and cultural centre. It is multicultural society with significant Afro Caribbean and Asian communities as well as a large Irish population. It is very much an industrial region whose prosperity is based on metal industries originally due to the locally available coal and iron ore.

It is said to have more canals than Venice and one has the incongruous juxtaposition of canals built in the late 1700s, modern telecommunications towers, a large number of Victorian Civic buildings but for the most part as seen from the air essentially non remarkable architecture much of it built in the 50s and 60s to allow for a new comprehensive road network and to replace the devastation caused by the bombing in the second world war.

On the night of Thursday November 21 1974 a duty reporter on the local evening paper received a coded message to say that a bomb had been planted in the Rotunda and at the Tax Office in New Street a few hundred yards away. The message was conveyed to the police but within minutes as they were arriving the bombs went off. The first was at the Mulberry Bush a public house on two levels built into the base of the Rotunda that had been the subject of terrorist bombs twice before. The force of the explosion blew out the contents of the pub onto the street, carpets, glass, furniture etc and killing several people and injuring many others. A passing bus had its windows blown out and was sufficiently damaged to be written off.

Further along New Street, one of the City's main thoroughfares was the Tavern in the Town. This pub was situated below street level with only a door opening onto New Street. The clientele were entirely young people and at the time of the explosion there were 100 people in the bar. I do not know if one can imagine the horror of being there - a big flash, an enormous blast, the lights going out, the ceiling falling in and furniture and debris being blown around with peoples clothes being blown from their bodies. In the two incidents 21 people were killed and 162 injured.

Subsequently explosives experts from RARDE reconstructing the events considered the two pub bombs to consist of about 30lb of blasting explosives for the force of them had blown holes a metre or so in diameter in the 10" thick concrete floors of both buildings. Painstaking examination of the debris revealed the remains of alarm clocks; batteries and D ring shackles suggesting the devices were concealed in a small briefcase or suitcase.

A third bomb was found later that night about a mile or two from the city centre at the rear of a Bank but it failed to go off. It was subject to a controlled explosion and it was found to consist of 13½lb of Eversoft Frangex gelignite made by Irish Industrial Explosives Ltd together with an alarm clock, battery, light bulb and Phillips cross headed wood screws exactly like 7 other similar bombs encountered in the Midlands region in the previous 16 days. One of those earlier bombs, of significance to subsequent events on the evening of November 14, had exploded prematurely at the Central Telephone Exchange in nearby Coventry killing the planter James McDade and drawing attention to his colleague Ray McLaughlin who was arrested running away from the scene.

Following the explosions in the pubs a watch was placed on all sea ports and airports and 5 Irish men were stopped for routine questioning at the port of Heysham in the north west from where a sea ferry service operated to Belfast. They had left Birmingham a quarter of an hour or so before the bombs had exploded, subsequently changed at Crewe onto the boat train from London. Although unknown at the time it subsequently emerged they had known McDade, two having gone to school with him and McDade had lodged with one of them and they were en route to attend his funeral in Belfast. Subsequently another with whom the five had been prior to the departure from Birmingham was arrested. The group have become since known to the world as the Birmingham Six.

At that time in the UK the technology available for dealing with explosive cases was limited. TLC was the favoured technique although GC was being used by some. John Lloyd had published his paper in 1967 on the detection of microgram amounts of nitroglycerine and related compounds and Jenkins and Yallop had published the use of TLC in the purely forensic science context for handswabbings in their 1970 in Explosivstoffe paper.

The Lloyd paper had an initial microchemical test on the suspect substance carried out on a microscope slide with confirmation by subsequent TLC. The nitroexplosive material being visualised by heating the plate after lightly spraying with caustic soda and then treating the cooled plate with so called Griess reagent - sulphanilic acid and α naphthylamine in acetic acid.

By way of digression since the Griess test as such has been clearly wrongly discredited in the eyes of the public it is perhaps appropriate to say a few words about him. Johann Peter Griess was born in Germany in 1829 the son of a blacksmith. He began his advanced studies in Kasel at the Polytechnic then went to Jena and Marburg. By all accounts he was a rebellious and idle student always in trouble with the authorities. After a period in a tar distillery in Offenbach he returned to Marburg to work under Professor Kolbe. His career was launched when A W von Hofmann who had been impressed with some of his earlier papers invited him to London. After three years of a well executed investigation he secured an appointment as chemist at a brewery in Burton on Trent a post he held until his death in Bournemouth, England in 1888. He became a fellow of the Royal Society and one of the founders of the Institute of Chemistry. His main contribution to chemistry was not in brewing but in the early discovery which Hofmann had noted - the formation of a new type of organic nitrogen compound by the action of nitrous acid on certain amines. Subsequent work showed that the diazo compounds produced - his term - would couple with other compounds thereby opening up the general way to a new class of synthetic coloured compounds. The Griess test in the context of explosive analysis as you know is based on the fact that nitrate esters will undergo breakdown under alkaline conditions to produce nitrite ions. These together with a mixture of sulphanilic acid and α naphthylamine in 30% w/v in acetic acid will result in the formation of a pinkish red coloration within about 10 seconds. The absence of a pink colour if the alkaline hydrolysis step is omitted establishes the absence of free nitrite in the original sample material.

Returning to the case, on that night of 21 November 1974 the officer in charge of the police station to where the five had been transferred asked that a forensic scientist from the local Forensic Science Laboratory come and undertake an apparently routine hand swab of the detained five before releasing them to continue their journey. The scientist had modified the published Yallop handswabbing method. His approach after thoroughly cleaning himself and his equipment was to take an ether swab of firstly one hand, squeeze out the ether into a porcelain bowl, add a little further ether and divide the sample into three. To one bowl he added caustic soda and Griess reagents, to the other he added just Griess reagents and the contents of the final bowl was retained for confirmatory tests. The process was repeated with

the other hand after which the fingernails were done. In the case of the five, the first two gave completely negative tests. The next gave a positive for one hand. The fourth individual gave negative Griess tests and the final one gave a strong test on the right hand. In the instances where a positive Griess test was obtained water swabs were taken and with two, positive tests for nitrate and ammonium ions were obtained. The nitrate was assayed using a modification of the Griess Test using metal and the ammonium using Nessler's. The sixth individual who did not travel on the train was subsequently detained in Birmingham and gave negative results using the standard Lloyd TLC technique.

Arising from the tests they were arrested and taken back to Birmingham where they underwent extensive questioning and in the course of time, a number made confessions.

After the tests at Morcambe the samples were taken back to the Laboratory but subsequent TLC failed to confirm the positives. Later on use of a then recently delivered GCMS machine at Aldermaston whilst not providing a total mass scan at the appropriate retention time did using single ion monitoring show a peak of m/z 46 at the appropriate time on one sample. The level was very low that the output appeared as a blip on an oscilloscope screen and on the pink UV paper used at the time.

Obviously extensive police work followed but in due course in June 1975 the trial was held at Lancaster Crown Court. The prosecution case was based on confessions, circumstantial evidence and the scientific findings. Clearly the tests results were important if the prosecution case was to succeed.

As Chris Mullin said subsequently in his book if the impact of results of the analytical tests could be reduced, the prosecution would have nothing on which to base the case but the confessions and circumstantial evidence. Confessions could be explained away by allegations of police violence. Association with known IRA men and the other circumstantial evidence of going to a funeral of an IRA man killed on duty was not in itself proof of guilt. If, on the other hand, the scientific evidence stood up, then the defence had a problem as there was no innocent straightforward explanation for being found on a train to Ireland with nitroglycerine on your hands a few hours after a bombing.

The forensic scientist told the court that, on the basis of the Griess tests alone, he was 'quite happy' that Messrs Power and Hill had been in contact with commercial explosives. 'What do you mean by "quite happy", he was asked. 'Ninety-nine per cent certain', was the reply. He was asked to explain why a sample which gave a positive reading on Griess should have given a negative reading on tests that were supposed to be up to a hundred times more sensitive but he had no firm suggestion other than evaporation as a possibility.

At the trial Judge and counsel alike appeared unknowledgeable on scientific matters and from the transcripts it is clear that the participants spent hours meandering back and forth between Griess tests, mass spectrometry and thin layer chromatography, ammonium and nitrate ions, nitrates and nitrites.

The defence called an ex HO Chief Inspector of explosives to rebut the evidence, however, whilst his evidence was sound it was discredited in the eyes of the court by virtue of the adversarial system and his having to acknowledge never having worked in a FSL or done any practical handswab analysis etc etc

After the 42 days trial the Six were found guilty of the offences as charged and sentenced to life imprisonment. The judge in his summing up described the forensic science as an absolutely critical in the case. He stressed that there had been a conflict over the forensic science evidence but that Chief Inspector of Explosives had produced no proof of the position he was forwarding.

The Six appealed and the case was heard on 30 March 1976 but in due course was dismissed.

The main argument centred on the fairness of the judges summing up. At this appeal the scientific issues attracted little attention. The Lord Chief Justice Lord Widgery saying in effect that whilst the scientific tests for explosives had given positive results for Power and Hill, a subsequent and one understands more precise and accurate test failed to confirm the original one and none of the other accused had any traces of explosives on their hands. Interestingly Widgery at one point said that the traces of explosive played such a small part'.

Having exhausted the available Appeal machinery it is difficult in view of the horror that the indiscriminate bombings produced in the minds of the average person to see how any campaign to review their cases could be initiated, but slowly from the beginning of the 1980s questions were asked. One of the most significant events must undoubtedly have been the World in Action investigative journalism type programme produced for Granada TV that was screened on 28 October 1985. It ranged far and wide over all the issues involved in the case. To look at the scientific aspects the researchers commissioned two independent forensic scientists to look at the Griess Test in some detail, namely Brian Caddy the Head of the Forensic Science Unit at Strathclyde University and Dave Baldock an ex government forensic scientist.

Their work supported what the retired Home Office Chief Inspector of Explosives had said at the trial that under the conditions of the test believed to be used by the scientist, that nitrocellulose will react. The Six had played cards on the journey to Heysham and Caddy was able to show that swabbing hands of individuals who had played with a pack of cards produced positive results.

Following the programme and the subsequent publication of Chris Mullin's book the campaign for the release of the six moved up a gear with the support of senior churchmen and other influential figures who continued to believe in the appellants innocence. On the scientific side the Head of the Forensic Science Service commissioned an indepth review including experimental work into the Griess Test by Dr Whistance and Mr Fereday two senior staff at the Home Office Forensic Science Laboratory at Aldermaston who reported in February 1986.

The Whistance Fereday work showed that:

The concentration of the sodium hydroxide used, the presence of organic solvent and temperature all dramatically affect the sensitivity of the reaction for NG.

They also confirmed the wide distribution of nitrocellulose containing material. Nitrocellulose-coated playing cards, nitrocellulose-based touch-up paints, furniture lacquers, clear lacquer, nail varnishes and magazine covers can all give positive responses to the Griess test at normal room temperatures using aqueous sodium hydroxide in the concentration range 0.1 - 10% as the hydrolysis reagent.

When viewed in conjunction with the results of the tests with nitroglycerine it is readily apparent that when a presumptive Griess test for nitroglycerine is conducted the test conditions must be chosen with extreme care to minimise possible interference from any nitrocellulose-based material(s) that might be present.

The case was referred back to the Court in 1987 by a reference from the Home Secretary. There were two grounds, the fresh scientific evidence I have mentioned carried out by Messrs Whistance and Fereday and an allegation made by a former police officer who claimed to have witnessed intimidation of the Six whilst they were in police custody. Dealing solely with the scientific issues much time was taken up at the hearing investigating the exact procedure followed by the scientist in 1974 as this was clearly crucial. The Whistance and Fereday work had demonstrated that if as was first thought, a solution of 1% caustic soda at room temperature had been used the positive results could have been due to contact with nitrocellulose especially

if ethanol was used either as the swabbing solvent or in the dilution of the sample. The scientist however claimed he used 0.1 % caustic at sub ambient temperature without ethanol under which conditions nitrocellulose could be excluded and the test becomes "specific" for nitroglycerine. There were pointers each way and in the event the Appeal Court held that there was so much doubt as to the procedures and in particular the strength of the caustic soda used, they could not safely regard the tests as specific. Much consideration in the hearing and subsequent judgement was given to the issue of the other contender being nitrocellulose, its selective persistence and failure to demonstrate it on the TLC.

However in the final analysis the court did not base its decision on the absence of possible sources for nitrocellulose but on the positive result for the GCMS of Mr Hill's left hand. At that Appeal, unlike the original trial the person who carried out the mass spectrometry work was called. She explained how the machine had been set up to monitor ion m/z 46 at a retention time of 4.2 minutes and how on that occasion she had not only analysed the Birmingham Six case swab samples but also ones from two other cases. In the Birmingham Six run the increase in m/z 46 seen on an oscilloscope was very small as opposed to small and large in the other two and she reported this as suggesting the possible presence of NG. In answer to another question she considered that m/z at 46 after 4.2 minutes as far as she was aware was consistent with NG. Alternative explanations were afforded for this by defence experts but at the end of the day the Court of Appeal decided that the presence of NG on Hill's left hand for which there was no innocent explanation was proved beyond reasonable doubt and the 1987 Appeal was dismissed.

The media campaign to secure the release of the Six continued unabated in spite of the Appeal result and following the DPPs decision during the course of the Guildford and Woolwich inquiry that he could no longer regard the Maguire convictions in a similar terrorist case as safe and satisfactory and Sir John May's subsequent conclusion in his interim report to recommend the Home Secretary to refer that case back to the Court of Appeal, a decision was taken after discussions between the FSS and the Department in the Home Office responsible for investigating alleged miscarriage cases that the FSS review the forensic evidence in the Birmingham Six case. This review led ultimately to the Home Secretary referring the case back to the Court of Appeal.

The review was undertaken by Dr J B F Lloyd, Dr M Stephenson, Mr M Fereday, Mr J Glaze and myself, and was based on the trial transcripts, remaining documentation and some further scientific work. The approach adopted was to try and establish exactly what the scientists did and to interpret that with the results of the further work to reach a view on the correctness of the conclusions drawn by the judges on the scientific evidence in this case.

It was recognised that the scientific work in the Birmingham Six case was undertaken some 16 years ago and the procedures, documentation and standards in use then were vastly different from today. Science has moved on significantly, standards of documentation, quality control and procedures for checking and reporting case examinations have changed enormously and equipment available today is far more sensitive and specific. Additionally a considerable amount of background research has been conducted over the years and the knowledge of the significance of findings have advanced following surveys and reviews. Forensic scientists of that time perhaps had a harder task in view of the limitations of the techniques and knowledge available to them as well as working without the benefits of any formal quality assurance backup procedures and often being required to use methods that had not been adequately validated. Nonetheless the scientists of that time like their modern counterpart signed their statements to the effect that "what they reported was true to the best of their knowledge and belief and in

making it if it was tendered in evidence they would be liable to prosecution if they wilfully stated anything which they knew to be false or did not believe to be true".

With the passage of time, as a result of the brief scientific casenotes and the absence of detailed documentation of the methods used, we had to rely in part on individuals memories as to exactly what was done. The evidence in chief and the subsequent cross examination of both forensic scientists provides a broad outline although it is deficient in certain critical areas that made our job reviewing the work objectively difficult if not impossible. The conclusions we reached were based on considering the fundamental issues involved in any analytical testing namely specificity, sensitivity and the reproducibility or reliability of the tests used.

The mainstay of the scientific aspects of the case was the version of the Griess test that produced positive tests on the swabs from Mr Powers right hand and Mr Hill's right hand.

A positive Griess test if an extract had been subjected to caustic soda hydrolysis is what you would expect if nitroglycerine were present but a positive Griess test in itself cannot be considered sufficient to lead to the conclusion that nitroglycerine is present.

In order to establish beyond reasonable doubt the presence of nitroglycerine we felt it is necessary to obtain positive results in two or possibly three further confirmatory tests. This was clearly not achieved in this case.

None of the original Griess test positive results were confirmed by any subsequent tests and the sample subjected to GC/MS was not previously Griess tested and post event testing proved negative.

Our practical work fully confirmed the earlier work of Whistance and Fereday particularly in relation to the sensitivities with the differing strength caustic soda solutions. Additionally there was the work done by John Twibell and others at CRE Aldermaston on the persistence of NG on hands. The Twibell results show a steep fall off of NG with time. As a consequence of the interval between when members of the six might have handled explosives ie prior to catching the train and the swabbing some ten hours later we considered that the amount of NG would have fallen by a factor of a thousand. Taking into account the lack of sensitivity of the test when using 0.1% caustic, the inefficiencies of the swabbing process and the fact that the method required division of the sample by 3, were NG to have been present at Morcambe in the early hours of morning those with positive results would have had near gram levels on their hands at the time of leaving Birmingham.

One chance observation that emerged during this work was that in the original trial the scientist had drawn attention to the fact that at one stage in the swabbing he was getting false positives. You will recall that his procedure employed reusable porcelain bowls which he cleaned with soap and organic solvents. John Lloyd discovered that many soaps especially the liquid ones contain nitrite and any residual amount would clearly react irrespective of the strength of the caustic soda employed.

One of the factors leading to the dismissal of the 87 Appeal was the mass spectrometry. Details in the transcripts are sketchy and discussions yielded little extra information beyond the evidence adduced that a single ion of the right retention time was present in the swab extract of Mr Hill's left hand. That for Mr Powers right hand proving negative. It may not have been appreciated that Mr Hill's left hand had not been Griess tested originally and so the only evidence was a single equivocal result.

The scientist was particularly careful in stating at the Appeal exactly what the findings were and only went as far as to say there was the possibility of nitroglycerine being present. It is a matter of surmise what significance this evidence had in the dismissal of the Appeal.

It is only when one compares the GC/MS equipment of the early 1970s with that of the 1990s

with its sophisticated data handling capabilities that one realises the technical advances that have occurred within the working life time of many of us here today.

We were able to analyse hand swabs from various individuals known not to have handled explosives and far from being a rare occurrence there were many eluted components having a peak at m/z 46 and some had a retention time similar to NG.

Additionally a detailed study of the surviving GC/MS charts from the actual day in question showed that there was a small m/z 46 peak in the background, the height of which may have been influenced by the analytical arrangement.

Supporting the assertion that NG was present the scientist advanced his identification of the presence of ammonium in a water swab and nitrate in another. Our researches demonstrated that the presence of ammonium is not uncommon; it was found in five swabs taken out of 38.

The exact details of the nitrate testing is not clear but on the basis of the evidence in the transcripts it seems questionable whether it would be able to distinguish between nitrate and nitrite. If that was the case and the five were known to have been smoking on the train to Heysham a positive test would in the circumstances be unremarkable.

Arising from this and the related document work done on the confessions by a Home Office document examiner this final Appeal of the Six was successful and the tumultuous scenes outside the Court were seen on TV screens around the world on Thursday 14 March 1991.

In the immediate aftermath the Home Secretary, announced the establishment of a Royal Commission to undertake an inquiry into every aspect of the Criminal Justice process from conduct of the police investigations to arrangements for dealing with alleged miscarriages of justice once normal appeal rights have been exhausted.

Although prompted by concern about wrongful convictions its terms of reference also embraced ways of achieving the speedy conviction of the guilty.

In many ways this case was atypical but is perhaps a convenient vehicle for us as forensic scientists to review our role in the criminal justice process.

Since that time we have moved a long way on. We are all to varying extents introducing quality systems and moving towards accreditation with the related certification of our staff. The Forensic Science Service has introduced a new form of statement that sets out the circumstances of the case as understood by the scientist the purpose for which the scientific work is carried out, the technical issues involved, the results, the conclusions and significance of the findings.

The problems we as a review team experienced arose mainly from lack of documentation and information about the procedures used. There was no detailed validation of the methods employed; little background survey information and the approach did not provide a permanent record of the results or allow for its confirmation by another qualified scientist. One can sympathise with the aim to assist the investigating officer by working in tandem with him but one has to weight this against the unsatisfactory aspects of working in a police station without adequate equipment or support from colleagues and the inevitable pressure exerted by the police for results. This later aspect is particularly pertinent in a case of major national significance like this one when massive police resources are geared up and waiting. The case also highlights the need to define in advance how cases are interpreted and exactly how they are reported when all the results are not as expected. In summarising these points there is an obligation on us not only to sign up to a quality standard for our work, laboratory organisation, accommodation etc such as ISO 25 but for us to be in a position to demonstrate clearly to the wider community what we have achieved and to make our systems more open and accessible. Crucial to this case was the science and we must publish what we are doing so that it can be peer reviewed and

assessed. We need to agree scientific standards and levels of proof for particular forensic applications.

Of the wider issues it was clear in this case that our other colleagues in the CJS may be ill prepared to deal with and often demonstrated in the most direct terms that they do not always understand the scientific issues and their limitations - there is without doubt a culture divide between us. Many of us work in an adversarial or accusatorial system and it may not be an ideal system to satisfactorily resolve disputes between experts. A related issue was the inability of the defence without access to suitable backup to mount scientific investigations to the level or depth that the prosecution can due to the lack of resources or even individuals with the necessary knowledge. In discussions with defence counsel in the Birmingham Six case it was clear that they felt they had limited time to mount a thorough review of a case, rarely was there complete disclosure and there was a feeling of too close a relationship between official forensic science and the police.

One of the dangers we need to guard against in the adversarial system is being drawn to overstate ones findings.

Forensic scientists are engaged in tasks whose results can have profound consequences both for society at large and individuals in particular. It is essential that they are impartial, conduct themselves with honesty and professional integrity, and remember that their primary obligation is to the interests of justice.

The UK FSS now undertakes work not only for the prosecution but also for the defence so that the benefits of up to date knowledge, equipment and resources are available to both parties in the litigation.

We have developed a Code of Practice which sets out clearly the roles and responsibilities of the forensic scientists. Under this code Forensic scientists must:

- Confine themselves within the areas of their professional competence, and ensure that their skills and knowledge are maintained at the appropriate level.

- Only employ methods of proven validity, utilising appropriate standards and controls.

- Make a full, contemporaneous and accurate record of all work undertaken. The record must contain sufficient information to enable the work to be reviewed for reliability and accuracy by another scientist versed in the relevant field.

- Review their findings critically, ensuring that any conclusions are consistent with all the information available to them, and that any limitations in the work or conclusions are clearly stated.

- Make available all information to any person having a legal entitlement to receive it, and also protect such information from improper disclosure.

- Conduct all their professional activities in a manner which protects the health and safety of both colleagues and public.

- Forensic scientists must recognise an obligation to maintain the standards of their profession. Where they become aware of any deficiency in the work of other forensic scientists, they should draw attention to such deficiencies so as to initiate appropriate corrective action.

In summary this case has focused if ever it was needed on the important role forensic science has in certain criminal cases and it has highlighted our responsibilities not only as to the techniques used but also the role we have as witnesses. Since 1974 we have come a long way however we feel as I have indicated that there is further work to be done in accreditation, research, validation and being more explicit and open about the methods and techniques we use and their limitations. Additionally there is the difficult area of the roles and responsibilities of

the expert witness and this can only be dealt with by adequate training, regular assessment and some form of a code of practice or ethics to guide their work.

A SCHEME FOR THE ANALYSIS OF EXPLOSIVES AND EXPLOSIVE RESIDUES IN JAPAN

T.Kishi, J. Nakamura, Y. Komo-oka and H. Fukuda
National Research Institute of Police Science
6, Sanban-cho, Chiyoda-ku, Tokyo 102
Japan

ABSTRACT. It may be a distinctive feature in Japan that improvised explosive devices are commonly used in criminal cases. These improvised explosives are inorganic explosives such as home-made black powder and chlorate explosives. Trace explosive residues were extracted from post-explosion debris with water. Water extracts were analyzed by ion chromatography to determine inorganic ions. Micro X-ray powder diffractometry is also used to identify chemical species. If necessary, the debris was extracted with ethyl ether and analyzed by gas chromatography with electron capture detection to identify organic components such as nitroglycerin. Capillary electrophoresis has recently been used as a new powerful technique for analysis of small ions such as chlorate and nitrate. These anions can be determined within 5 min. The analysis of inorganic ions are very important to identify Japanese improvised explosives.

1. INTRODUCTION

Many forensic scientists have investigated criminal bombing cases and analyzed explosives and explosive residues from the crime scene. The analytical schemes employed by each laboratory staff are almost the same methods but differ in the details, because of their distinctive features[1-9]. During the past 3 years, a small number of bombing incidents occurred in Japan. It may be distinctive feature in Japan that improvised explosive devices are commonly used in criminal cases. These improvised explosives are inorganic explosives such as home-made black powder and chlorate explosives. There are few cases of commercial explosive such as dynamite.

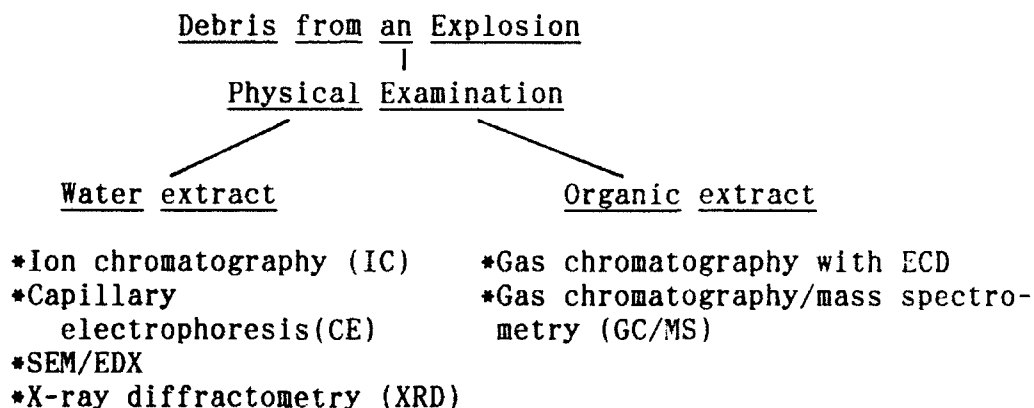
Therefore, the analytical methods for inorganic compounds are very useful to analyze explosives and their residues. The analytical scheme employed by our laboratory staff is described.

2. SCHEME FOR ANALYSIS

For the identification of home-made explosives, visual examination of debris is a very important step in the analysis scheme, because the size of the fragments gives an indication on the power of the explosives. Also fragments of the initiation device, such as ignition heater of gas cooking stove or electric detonator provide important information on the explosive.

The methods used routinely in the analysis of explosives and their residues were ion chromatography(IC), scanning electron microscopy with energy dispersive X-ray analysis(SEM/EDX), micro X-ray diffractometry(XRD), thin layer chromatography(TLC), capillary gas chromatography(GC), gas chromatography with electron capture detection(GC-ECD), gas chromatography/ mass spectrometry(GC/MS) and Fourier transform infra-red spectroscopy (FT-IR) with microscope. Capillary electrophoresis(CE) has been recently used as a new powerful technique for the analysis of inorganic ions.

For the analysis of organic component, GC-ECD and GC/MS are mainly used. For the analysis of inorganic component, IC, CE, SEM/EDX and XRD are used as follows.



2.1 Ion chromatography

Ion chromatography is used for separating and quantitating inorganic ions.

Figure 1 shows the separation of standard anions. Chloride, chlorate, nitrate and sulfate ions were separated and identified within 8 min.. However perchlorate anions should be separated under other analytical conditions.

Figure 2 shows the separation of standards cations. Sodium, potassium and ammonium ions were well resolved within 11 min..

In the actual case, we can determine potassium, nitrate, nitrite and sulfate ions from the explosion residues of black powder.

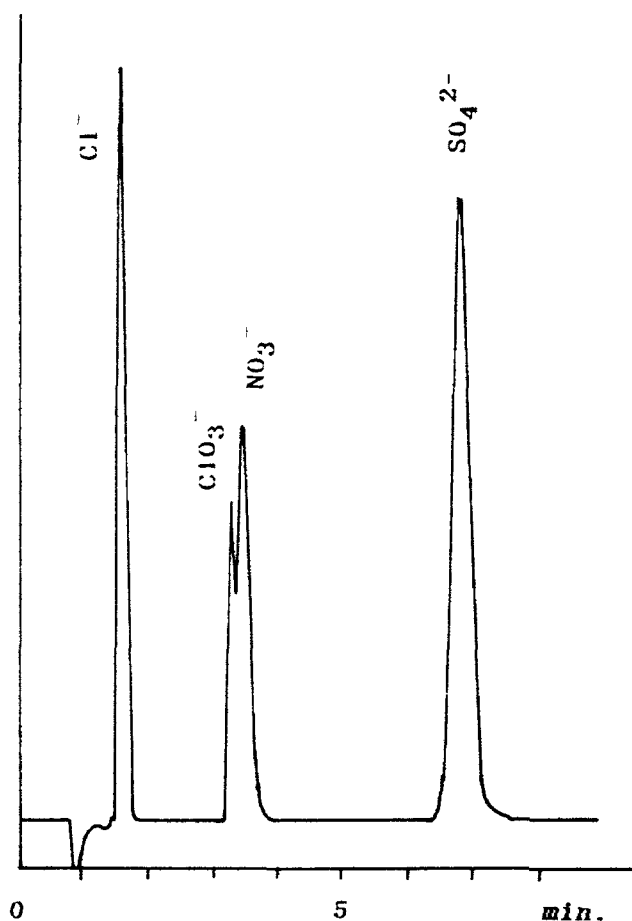


Fig.1 Ion chromatogram of anions
in the standard solution
Apparatus: Dionex 4000i;
Eluent: 1.8 mM sodium carbonate
+ 1.7 mM sodium bicarbonate
Column : AS4A
Suppresser: AMMS-II
Flow rate: 2.0 ml/min.

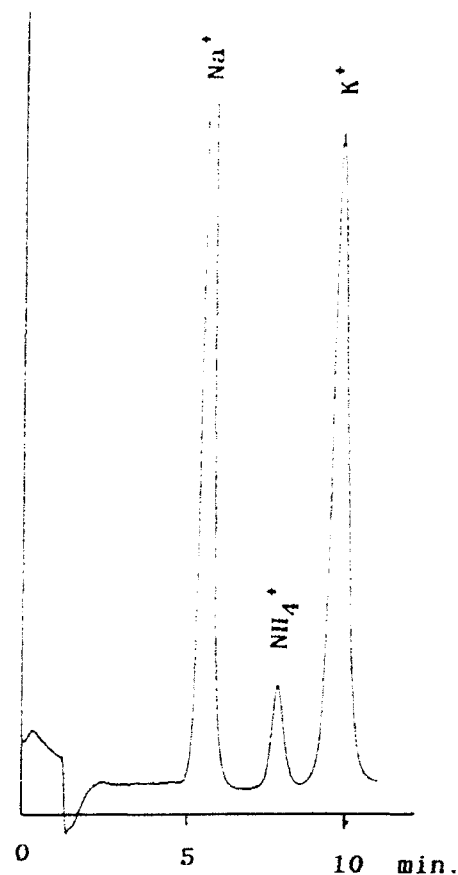


Fig.2 Ion chromatogram of cations
in the standard solution
Apparatus: Dionex 4000i;
Eluent: 0.02M HCl
Column: CG3-CS3
Suppresser: CMMS-II
Flow rate: 1.5 ml/min.

2.2 SEM/EDX

SEM/EDX is useful for elemental analysis. For example, we can detect potassium and sulfur in the residues of black powder.

2.3 X-Ray diffractometry

It is often necessary to fully identify the explosive. X-ray diffractometry was used to identify their chemical species.

For example, we can identify potassium nitrate and sulfur in the black powder from their patterns.

2.4. Capillary Electrophoresis

Capillary electrophoresis has recently been used as a new powerful technique for analysis of small anions (chloride, chlorate, perchlorate, sulfate, nitrate etc.) and cations (sodium, potassium and ammonium).

Apparatus and procedure.

Experiments were conducted by using a Waters Quanta 4000 system that consisted of a 0-30 kV power supply, autosampler, and UV absorbance detector. The injection system of this instrument consists of the hydrostatic and electro modes. The light source is a Hg lamp. Polyimido-coated fused silica capillary tubing (75 μ m diameter, 60 cm length), was used as a column.

For anion analysis, hydrostatic injection for 30 seconds was used and -20kV was supplied to the column. The detection wavelength was 254 nm. Electrolyte used was 5 mM chromate and 5 mM Nice-Pak.

For cation analysis, the applied voltage was 30kV after 10 seconds gravity injection. The detection wavelength was 214nm and the electrolyte used was 5 mM UVcat1.

Standards. Stock solutions of the standards of ions were prepared to be 1000ppm in water. These standard solutions were mixed and diluted to 5 ppm.

Forensic sample. Chlorate explosive, which was made by mixing potassium chlorate, sulfur and charcoal, was charged into a steel pipe and ignited by an electric detonator. The bomb fragments were collected and extracted by water. Water extract was used for analysis of ions.

Figure 3 shows a separation of 7 anions of interest in inorganic explosives. All are well resolved. Analysis time is only 3 min. Figure 4 shows a separation of 3 cations (potassium ion, sodium ion and ammonium ion). These cation are also well resolved within 2 min. Approximate detection limits were determined from concentration studied and were founded to be ppm levels for each ion. If the electro injection mode was used, detection limits were in the ppb range.

Figure 5 shows the water extract of bomb fragments analyzed with capillary electrophoresis. Chloride and chlorate, which originated from potassium chlorate, were found. Sulfate, which originated from sulfur, was also found. Sensitivity of this method was enough to determine these ions from the fragments.

Therefore, capillary electrophoresis is used as a complementary technique to ion chromatography for the analysis of small inorganic ions.

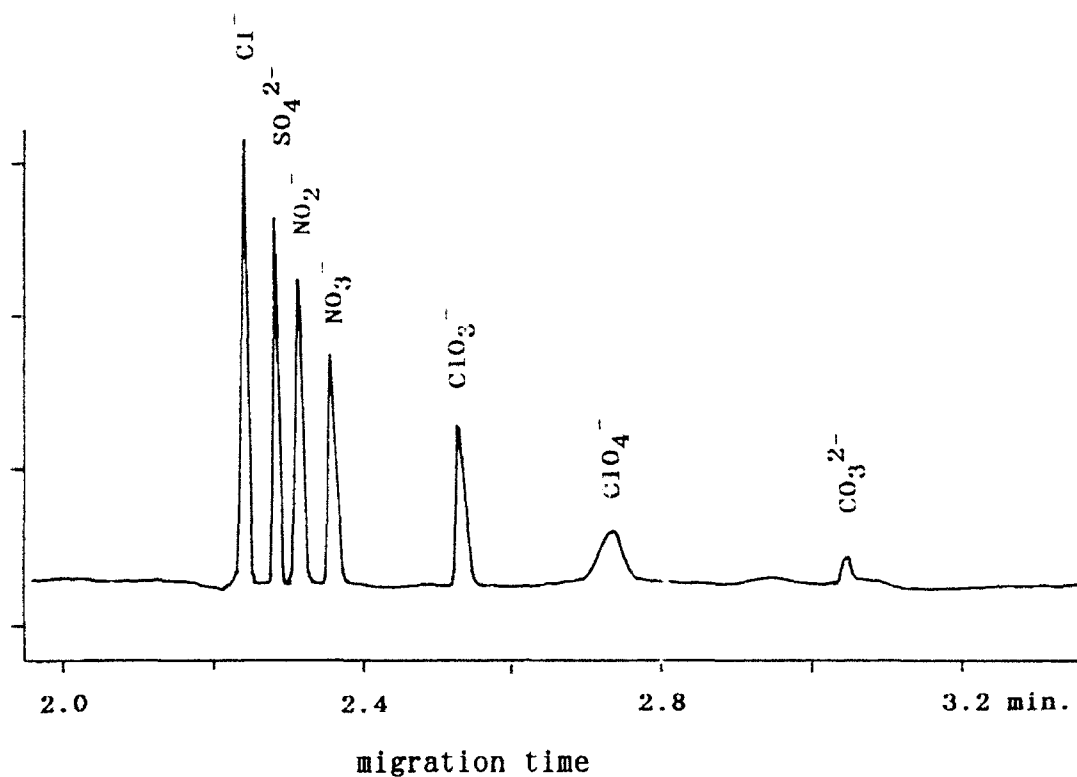


Fig.3 Capillary electrophoretic separation of anions in the standard solution

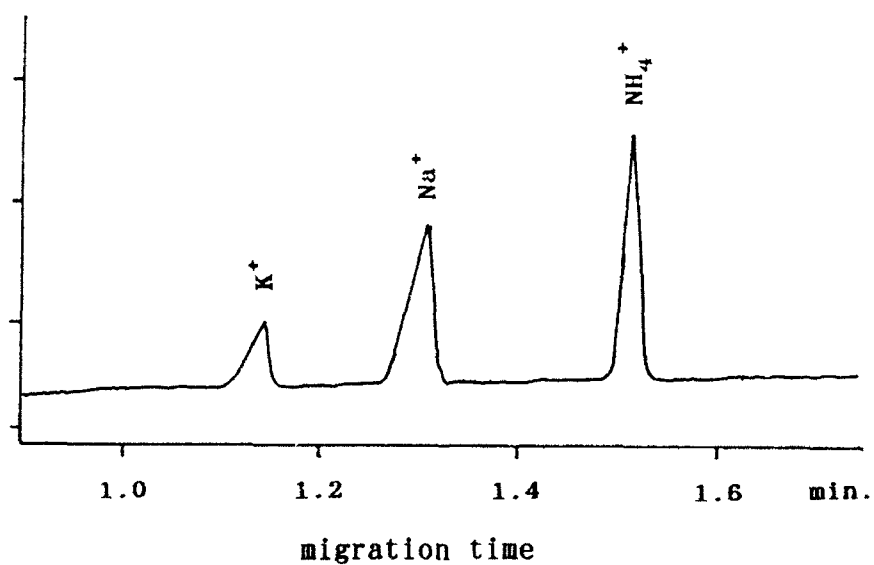


Fig.4 Capillary electrophoretic separation of cations in the standard solution

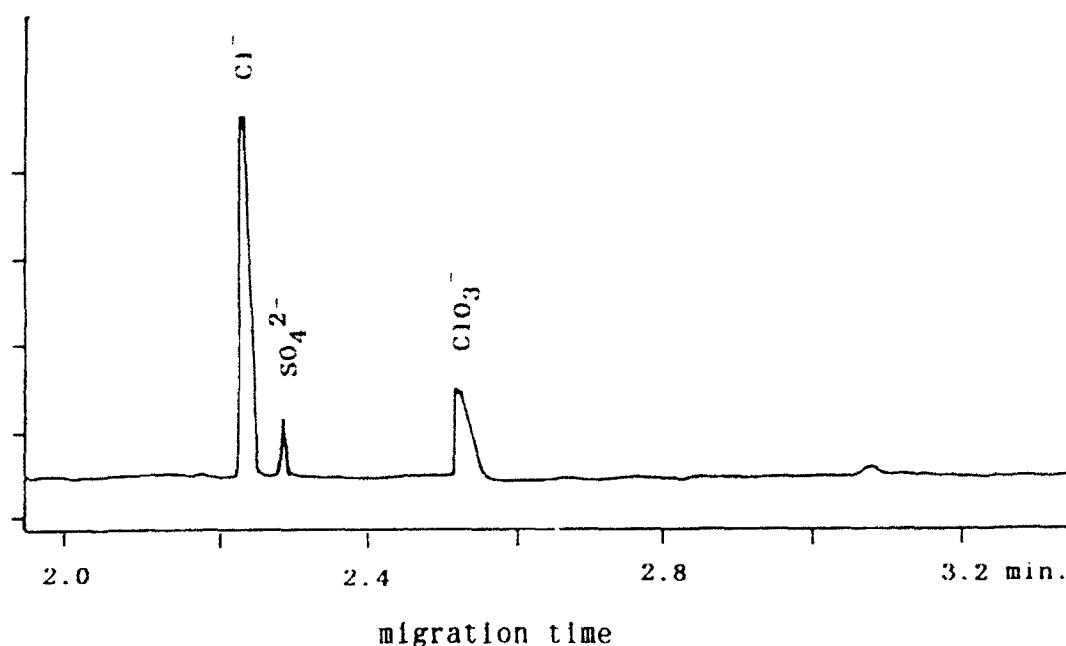


Fig.5 Capillary electrophoretic separation of anions in the water extract of explosion debris

This technique has also been used for separation of organic explosives[10]. Capillary electrophoresis will therefore be applied to forensic analysis because of its short analysis time, high resolution and small sample requirements.

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ANTIBODY-BASED FIELD TEST KITS FOR EXPLOSIVES

Dean D. Fetterolf, Ph.D.
FBI Laboratory
Forensic Science Research Unit
FBI Academy
Quantico, VA 22135

ABSTRACT. An enzyme-linked immunosorbent assay (ELISA) developed for the detection of Trinitrotoluene (TNT) in munitions wastewater has been adapted to the detection of TNT residue on hands following contact. Using the procedure developed, as little as 50 pg of TNT could be detected. Accounting for sample size and dilution, the 50 pg equates to 15 ng of TNT recovered from the hands. Following contact with TNT, amounts ranging from 53 ng to more than 1500 ng were recovered from hands. The monoclonal anti-TNT antibodies showed no cross-reactivity with several other explosives or common contaminants. A latex bead agglutination assay has been developed which has detected as little as 25 ng of PETN. This agglutination assay is complete in 30 seconds and is being incorporated into a disposable field test kit.

1. Introduction

Increased terrorist activity in the recent years, has prompted the need for new and improved methods for the detection and identification of explosives. The initial goal of this research was to adapt an enzyme immunoassay developed for TNT in munitions wastewater to forensic use. The use of immunoassays in forensic science are typically associated with urine drug testing and serological examinations. An excellent review of enzyme immunoassay techniques and theory has been published (1). The initial effort was centered around the development of an appropriate sampling procedure for TNT on hands. In addition, we evaluated the sensitivity of a latex-bead agglutination assay for PETN.

The persistence of military and commercial explosives on hands following contact is well documented (2-5). Explosives test kits using modified Griess reagents have been used to detect nitro- containing explosives on hands and surfaces (6-7). Although sensitive to nanogram amounts of explosives, such nonspecific chemical screening tests are subject to potential cross reactivity or interference from nonexplosive substances such as synthetic nitro musks (8). For this reason, a well-trained user of field test kits will have the results confirmed by more specific laboratory tests, such as gas or liquid chromatography.

In order to improve the specificity of the screening tests, we chose to undertake the evaluation of a new and innovative method of detecting explosives, the use of antigen-antibody reactions.

1.1 TNT ELISA ASSAY

Figure 1 shows a schematic diagram of the TNT ELISA assay procedure. This procedure was adapted from an ELISA procedure developed by Westinghouse Bio-Analytical Systems (WBAS) (Rockville, MD.) for the detection of TNT in munitions wastewater.

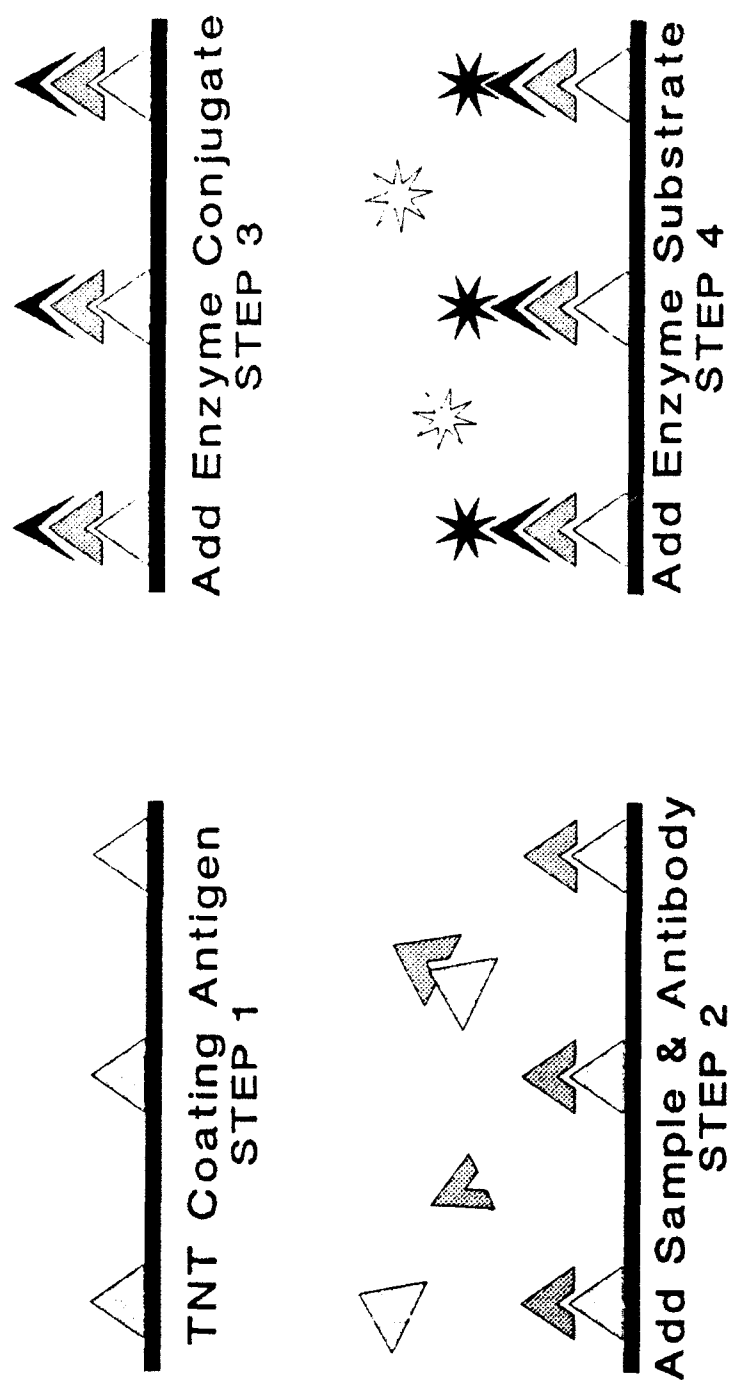


FIGURE 1. Basic enzyme-linked immunosorbent assay (ELISA) principles.

Step 1 of the immunoassay procedure involves precoating the plate with a TNT-protein conjugate that adheres to the well surface. In Step 2 competitive inhibition occurs when samples containing TNT are incubated with mouse anti-TNT antibodies. The antibodies can either bind to the free TNT in the samples or to the TNT bound to the surface of the well. After an equilibrium is reached the plate is washed and the antibodies bound to the free TNT are washed away leaving the antibody bound to the immobilized conjugate. Therefore, the amount of antibody bound to the well is inversely proportional to the TNT concentration present in the sample. The greater the concentration of TNT in the sample the less monoclonal antibody is available to the immobilized TNT conjugate.

In Step 3 the plate is incubated with goat anti-mouse (μ -chain specific)-alkaline phosphatase conjugate which binds only to the surface-bound mouse monoclonal anti-TNT antibodies. The plate is washed again. In Step 4 the enzyme substrate is added. The surface-bound enzyme-antibody conjugate converts the colorless substrate to a yellow product. The color is directly proportional to the amount of TNT monoclonal antibody bound in each well and, therefore, is inversely proportional to the amount of TNT in the sample.

This successful TNT laboratory assay required approximately 3.5 hours and a skilled technician to complete, thus making it too cumbersome and time consuming as a general purpose field test. Meanwhile antibodies to PETN were under development and a new assay procedure was being explored.

1.2 PETN LATEX BEAD AGGLUTINATION ASSAY

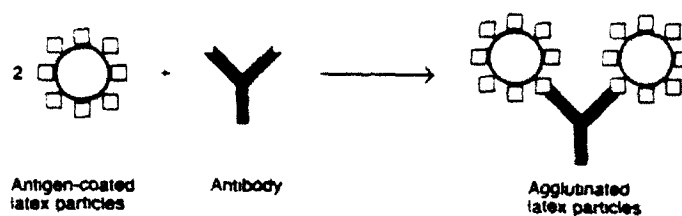
In a separately funded effort, Westinghouse's Law Enforcement Products Division (Baltimore, Md.) has developed an antibody based method for PETN using a latex-bead agglutination technology. Agglutination reactions are widely used throughout the biochemical community for the detection of small quantities of proteins and drugs in physiological fluids. The PETN assay has been reduced to 30 seconds. The sample collection device and assay are being incorporated into a disposable item which is analyzed using a reusable hand-held spectrophotometer.

Figure 2 shows the basic steps in the PETN agglutination assay. In Step 1 of the assay agglutinated latex particles form when the latex particles ($< 1 \mu\text{m}$ particles) which have covalently bound to their surface the analyte of interest are mixed with the specific antibody. Because of the multiple binding sites on both the latex particles and the antibody a crosslinking or polymerization of many particles occurs in Step 2. As shown in Step 3, in the presence of the analyte of interest this agglutination is inhibited. This agglutination reaction can be monitored both visually and electronically in about 30 seconds. PETN antibodies from one particular rabbit showed detection as low as 30 parts per trillion using an ELISA assay similar to the TNT assay. Recent preliminary results of the agglutination assay have demonstrated a detection of 25 ng of PETN.

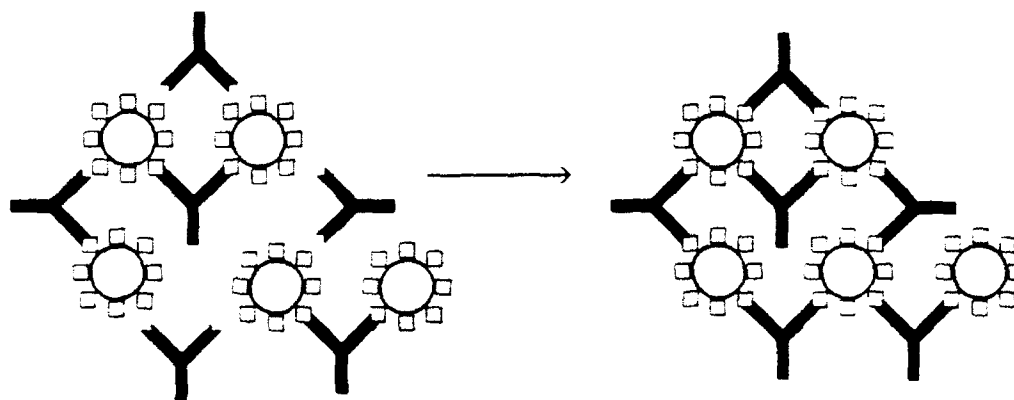
2. Materials and Methods

2.1 TNT ELISA PROCEDURE

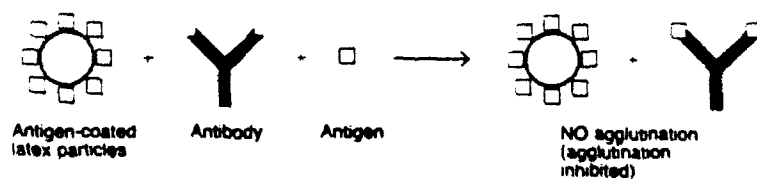
The TNT ELISA procedure has been previously described in detail (9) and is abbreviated here. Ninety-six well, flat bottom, high binding microtiter plates (Costar, Cambridge, MA)



STEP 1. In latex agglutination: Antibody linking of two particles.



STEP 2. Antibody cross-linking of many particles.



STEP 3. Inhibition of latex agglutination by free antigen.

FIGURE 2. Basic latex-bead agglutination principles.

were coated with reconstituted Westinghouse Bio-Analytical Systems (WBAS) TNT coating antigen. Fifty microliters of sample and TNT standards ranging in concentrations from 0.33 ppb to 100 ppb were loaded in triplicate into the wells. Six wells were reserved for controls. The three negative antibody control and negative TNT controls were also carried out. The plate was covered and allowed to incubate for one hour at room temperature. After incubation, the plate was washed five times with PBS-T and firmly slapped dry.

The antibody-enzyme conjugate was added to each well. The plate was covered and incubated at room temperature for 30 minutes. After the incubation the plate was washed with PBS-T and slapped dry as before. Then 100 μ l of the phosphatase substrate solution was added. The plate was read at 405nm after the positive control had reached an absorbance of at least 0.8 on a Dynatech MR600 microplate reader (DYNATECH Laboratories, Inc., Chantilly, VA). A typical calibration curve shown a linear response was from approximately 1 to 100 ppb TNT with a correlation coefficient of 0.997. For example, 50 μ l of a 1 ppb solution of TNT corresponds to 50 pg TNT. For a 1:300 sample dilution this equates to a total 15 ng recovered from the hands.

2.2 PETN LATEX AGGLUTINATION PROCEDURE

The latex agglutination assay for PETN was carried out in the plastic apparatus from a Roche Abuscreen ONTRAK™ cocaine drug abuse urine testing kit. A sample is placed in the mixing well with the antibody reagent, a reaction buffer and the latex reagent. The stirred mixture then moves along a track on the kit by means of capillary action.

The rabbit PETN polyclonal sera is diluted 1:100 in antibody dilution buffer (25mM Sodium phosphate, pH=7.4; 1mg/ml bovine serum albumin (BSA) and 0.1% sodium azide). Samples to be analyzed are also diluted with this buffer reagent.

The reaction buffer contains 200 mM of a proprietary sulfonate reagent, pH=7.5; 4% Dextran and 0.1% sodium azide. The polystyrene latex particles of 0.285 μ m (microns) were coated with the PETN-protein conjugate by passive absorption. The latex reagent was diluted to 1.0% solids in the final concentration.

The agglutination reaction are performed by the sequential addition of 50 μ l of each reagent. The three liquids are mixed thoroughly and guided into the thin track opening. Once the mixture begins to flow by capillary action, the test proceeds on its own. After the solution has reached the viewing window the result can be visually determined.

3. Results and Discussion

3.1 RECOVERY OF TNT FROM HANDS

A series of hand blank samples from six individuals were assayed following the TNT procedure. These individuals had no contact with TNT or other explosives prior to the sampling. Table 1 shows the results of the hand blank study in which negative TNT controls and negative antibody controls were also analyzed. It was observed that at sample dilutions of 1:300 or greater an identical response to the negative TNT control was obtained.

TABLE 1. Hand Blank Results at a Dilution of 1:300

Sample	n	Absorbance	Std. Dev.
Negative Antibody Controls	3	0.007	0.002
Negative TNT Controls	3	0.828	0.061
Hand Blanks	12	0.821	0.058

Five individuals were instructed to handle the quarter-pound stick of TNT and rub their hands together. Samples were taken by swabbing the hands prior to and following contact. For the purposes of this initial study, the most efficient means of quantitative recovery from the hands was not investigated. Table 2 shows the semiquantitative results from this assay. Accounting for sample size and dilution the amounts of TNT recovered from the hands ranged from 53 ng to more than 1500 ng.

TABLE 2. Amount of TNT recovered from hands.

Individual No.	Left Hand, ng	Right Hand, ng
1	53	300
2	165	180
3	900	> 1500
4	225	160
5	135	85

The effect of hand washing was also studied. In this test, a subject handled TNT and rubbed her hands together as before. The samples taken immediately after washing with water were positive for TNT. Samples taken after washing with soap and water were negative. While not all soaps may be effective and the amount and method of hand washing can vary greatly among individuals these results suggest water alone may not remove all the TNT residue from hands but thorough washing with soap and water may.

3.2 SELECTIVITY - CROSS REACTIVITY OF TNT ANTIBODIES WITH OTHER EXPLOSIVES

In order to determine the specificity of the monoclonal anti-TNT antibody, a series of experiments were undertaken to evaluate the cross reactivity with other explosives under similar handling conditions. Each subject handled one of the explosives listed in Table 3 and was instructed to rub their hands together. Left- and right- hand samples were taken again. The cotton was removed from the swabs and added to water/sample buffer solutions. All of the samples were diluted 1:300 and assayed according to the procedure above. All hand blanks provided a negative response. No cross reactivity was observed between the monoclonal anti-TNT antibody and the six explosives tested. For these qualitative assays,

samples falling within the linear portion of the curve were simply called positive (+). Those exhibiting a response consistent with maximum color development (< 1 ppb TNT) were called negative (-).

TABLE 3. Cross reactivity with other explosives.

Explosive	Results, L/R
Semtex	-/-
Atlas 7-D	-/-
C4	-/-
Flex-X	-/-
Unigel	-/-
PETN	-/-

3.3 SELECTIVITY - EFFECT OF CONTAMINANTS ON TNT ASSAY

Musks, as well as a number of other chemicals, are known to present potential interferences with chemical or instrumental means of explosive detection. For example, synthetic nitro musks are similar in chemical structure to TNT and are common fragrance additives in toiletries. To determine the effects on the assay, 100 μ l of 2 undiluted musk perfumes were added directly to the microtiter plates in triplicate. This large concentrated sample of musk is likely to be much more than would be obtained from a hand swab. In these cases some inhibition of color development was observed. This may be due to partial stripping of the coating antigen from the plate or binding to the monoclonal anti-TNT antibody. Further studies are needed to elucidate the exact mechanism of this interference.

As shown in Table 4, when diluted 1:300 or greater the samples were observed to be negative. Gasoline, hand lotion and mouthwash were also applied to hands and recovered using the prescribed method. No effect on the assay was observed for these items. A small piece of wintergreen smokeless tobacco was extracted and added directly to the well. The extract was visibly cloudy thus affecting the absorbance measurement.

TABLE 4. Response of TNT assay in presence of contaminants.

Sample	Alone (L/R)	TNT Added
Musk No. 1	-/-	+
Musk No. 2	-/-	+
Hand lotion	-/-	+
Gasoline	-/-	+
Tobacco	*	*

*Unfiltered Sample was cloudy upon addition to well.

As shown in Table 4 another test was performed to determine if the diluted contaminant would prevent a positive response in the presence of TNT. In this test a 100 ng of TNT standard was added to the wells in addition to the diluted contaminant. The assay showed a positive response for TNT in the presence of the musks, hand lotion, gasoline, and mouthwash. As previously mentioned the tobacco extract was cloudy. Filtration may be necessary for samples containing particulate matter.

3.4 PETN LATEX BEAD AGGLUTINATION ASSAY RESULTS

A series of rabbits and mice were inoculated with PETN-protein conjugate and antibodies were recovered using traditional procedures. ELISA assays of the PETN antibodies showed sensitivities ranging from 1 ppm in one mouse to as low as 30 ppt in one rabbit. The rabbit antiserum was used for all subsequent experiments. A series of standards ranging from 1000 ng to 25 ng were analyzed using antibodies diluted 1:50 and 1:100. Table 5 shows the results for the visual determination of whether or not agglutination had been inhibited. At a 1:100 dilution as little as 25 ng of PETN could be detected.

TABLE 5. PETN agglutination assay sensitivity.

Amount PETN (ng)	1:50 dilution	1:100 dilution
1000	+	+
500	+	+
100	+	+
50	+	+
25	+/-	+
0	-	-

Some difficulty existed in the visual interpretation of the reaction due to the small size of the latex particles used. Work is progressing towards using a larger particle. In addition, a battery operated hand held spectrometer has been developed which will use measure the optical density. In addition, all reagents have been incorporated into a self contained, single use kit.

4. Conclusions

The results indicate that an enzyme immunosorbent assay developed for the detection of TNT in munitions wastewater was successfully adapted to the detection of TNT on hands. These results indicate that the mouse monoclonal anti-TNT antibody for TNT is specific for TNT and shows no cross reactivity with those explosives or interferant tested in this study. The assay was capable of detecting as little as 50 pg TNT.

The preliminary results from the PETN latex-bead agglutination assay indicate that it is possible to reduce the 3.5 hour laboratory assay into a 30 second field assay. Work is now under way to incorporate the agglutination reaction into a disposable field test kit. Continued development of monoclonal antibodies to other explosives should lead to future developments in this new area of explosives detection.

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Smokeless Powder Characterization An Investigative Tool in Pipe Bombings

CYNTHIA L. WALLACE and CHARLES R. MIDKIFF Jr.
*National Laboratory Center
Bureau of Alcohol, Tobacco and Firearms
Rockville, Maryland 20850*

ABSTRACT. Smokeless powder is the filler in more than 50% of U.S. pipe bombings. The physical and chemical characteristics of smokeless powder may indicate manufacturer, identify the specific powder used, or link powder in a suspect's possession to that in a bomb. Since the manufacturing and blending processes have a significant impact on forensic comparisons, effects of sampling and lot-to-lot variation will be examined. Changes in manufacturing and marketing can date a smokeless powder. This information may be used to provide investigative leads or associative evidence in a pipe bombing.

Introduction

Since the 1970's, criminal bombings in the United States have exhibited a significant increase in the use of low explosives. In our laboratory, about 50% of the explosives cases examined involve pipe bombs, and at least half of the pipe bombs our laboratory system examines contain smokeless powder. In the United States, there is wide interest in sport shooting with many shooters reloading their own ammunition. As a result, despite restrictions on explosives, reloading powders remain widely available for purchase by gun enthusiasts. Since 1987, we have maintained a library of canister smokeless powders. Selavka et al [1,2], described the ATF Smokeless Powder Database, and this paper presents an extension of that work.

The ATF Laboratory Smokeless Powder Data Base Approach

Because of our involvement in the investigation of criminal bombings, the ATF laboratories need to effectively identify smokeless powders. In 1976, Midkiff and Washington [3] described an approach based on particle appearance and morphology, determination of base, and presence of colored identifier particles. In 1978, Zack and House [4] measured the particle size of non-spherical powders and obtained good discrimination of different powders. At the FBI, a database library of capillary GC/MS data on chloroform extracts of 100 powders was prepared. The total

ion chromatogram (TIC) pattern of an unknown powder was compared by computer search with those in the database to provide potential candidates for subsequent morphology comparison and identification [5]. In 1988, Selavka et al [2], following the lead of Zack and House, described an approach for product identification based on classification by morphology and precise measurement of particle length, diameter, thickness and web thickness. A searchable database gave good results for non-ball type powders but ball types were more difficult to classify. This approach was updated [1] and extended by additional chemical characterization and an improved search routine. Ion Chromatography (IC) and GC/FID examination of ball-type powders were added to improve discrimination of this morphology type. These techniques detected a drying agent (Na_2SO_4), a flash suppressor compound (KNO_3 or K_2SO_4), dibutyl phthalate plasticizer and ethyl centralite, a stabilizer which also functions as a plasticizer at higher concentrations. With continual extension by additional work in our laboratory, a searchable database approach forms the basis for identification of smokeless powders in the ATF laboratories.

Since 1989, additions to our systematic identification approach include separate records kept on each lot of powder in our collection, continued work on analytical techniques to obtain chemical information, and the incorporation of additional information for refining identification or exclusion. Currently, the database contains information on 117 different powders representing 195 lots. Because of its size and complexity, the smokeless powder data file is maintained using the commercial database manager: R-base.

A major expansion of the database is the storage of information, other than that forming the basis for search and retrieval of candidate powders. A COMMENTS block in the data file contains additional information, from a variety of sources, about the product. Results from laboratory analysis of a product are recorded to indicate the range of variation which may be encountered. Physical differences observed in the product, such as changes in morphology or particle dimensions, dates of introduction or discontinuance of the product, or changes in the producer of the product are included.

Morphology groups

The first step toward identifying an unknown powder is to classify the particles into one of the following morphology groups as described by Selavka et al: Disc, Perforated Disc, Tube, Ball, Flattened Ball, Agglomerated Ball, Ciamp, or Lamel. The morphology category, Rod, has been eliminated. A canister powder may contain more than one particle morphology.

The powders that were originally classified as Rod, such as IMR 7828 and Norma N205, are actually Tubes with the perforation obscured by coating and glazing material. To measure the web on these tubes, the particle is scored, then broken in half, making the perforation visible and enabling its web to be measured. According to IMR Powder Co., the perforation is not sealed intentionally but may close over occasionally during the coating step. In the lots of powder we have examined, practically every particle had the perforation obscured. It remains to be seen how this phenomenon reproduces from lot-to-lot.

Some morphology groups are much more common than others. For example, we have 21 brands of Disc powder and five brands of Perforated Disc; however, four of these are obsolete and IMR

PB is the only Perforated Disc currently marketed. Agglomerated Balls are added in small percentages to four brands from Accurate Arms Co., only one obsolete brand consists solely of agglomerated balls (Winchester Western AA20S).

Measurements

Dimension measurements must be as accurate and reproducible as possible for effective search of the stored data and several enhancements have been made.

PARTICLE SELECTION

When measuring known powder or if a large quantity of questioned powder is recovered, judgment is required in selecting the particles to be measured. The presence of smeared particles or those distorted with scrap should be noted but not measured. A variety of particles that represent the designed characteristics should be selected. For example, with a Disc powder a representative group with the variety of thicknesses and diameters present should be chosen, if only the most perfect particles are selected, the result may be a thickness greater than that of a representative sample.

OBTAINING PRECISE MEASUREMENTS

Certain practices improve the reproducibility of measurements. For measuring webs with Tubes and Perforated Discs, a perfectly centered perforation is not necessary. By measuring web thickness on either side of the perforation and averaging, the resulting value reflects the true web thickness and eliminates problems encountered with off-center holes. Experiments measuring the diameters of Tube powders show the same average is obtained when measuring the diameter with the particle lying on side or on end, but that the standard deviation was much smaller with the particle lying on its side. With the particle on end, scrap from cutting introduces variability into the measurement.

Examination of additional lots or larger samples of a number of powders indicates the range of variation in measurements to be somewhat larger than originally indicated. A typical example is the diameter for Winchester Western WW231: 70 particles measured for one lot gave an average of 1.02mm with a standard deviation of 0.14mm, 20 particles measured from second lot gave an average of 1.17mm and a standard deviation of 0.12mm. When the lots are combined, the average is 1.05mm and the standard deviation is 0.15mm. As a result, the "size envelope" is being expanded to accommodate this variation as additional lots are measured. Although the effect is to reduce discrimination, the expansion is essential to reduce false eliminations.

MEASUREMENT SIGNIFICANCE

When searching measurements against the database, a knowledge of manufacturing practices is relevant. For example with Ball type, particularly with Olin BALL POWDER® which is produced in a unique continuous process, more confidence may be placed in the thickness measurement which

is determined when the powder is run through rollers than in the average diameter which, though useful, is a sieve fraction.

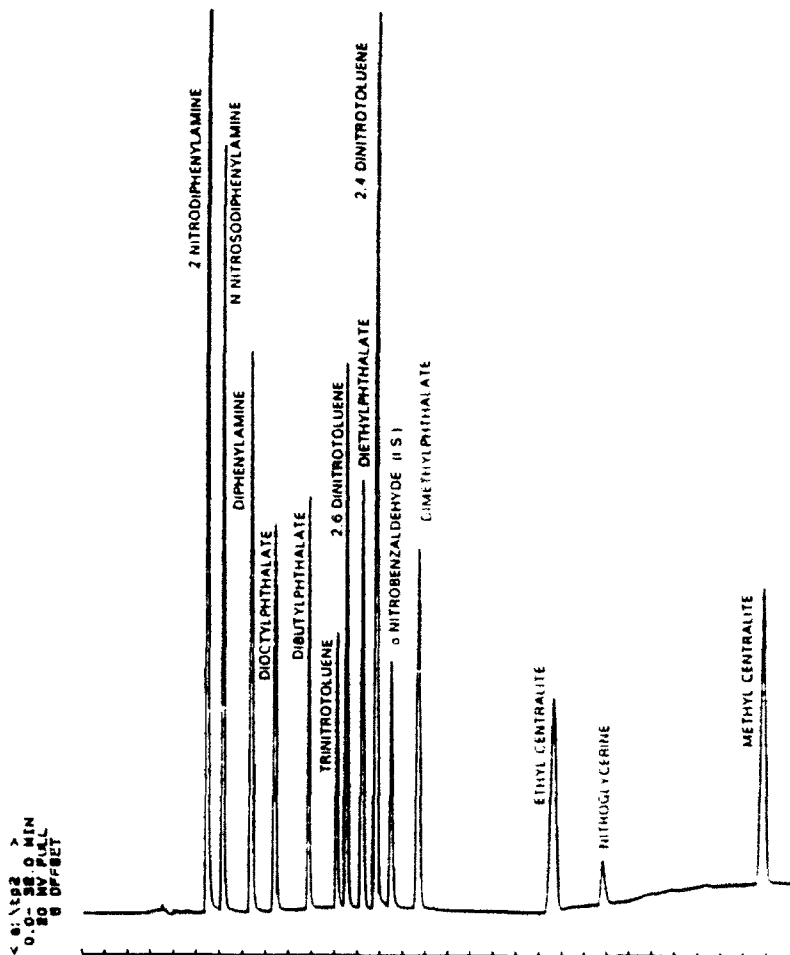
Likewise, the diameter of a Tube is more reproducible than the length due to the extrusion process. The diameter is determined by the die, but the length of cut is determined by the feed rate of the strands, the number of blades on the rotating cutter, and rotation speed. Slippage in the feed rollers, or a strand of powder that sticks or drags can affect particle length.

Chemical Analysis

Although we had initially evaluated GC/FID for the determination of several ingredients in smokeless powders, we are now using a more versatile gradient HPLC technique developed by Edward C. Bender of our laboratory. With this technique, we are able to simultaneously determine a number of deterrents, plasticizers and stabilizer derivatives which are useful in discrimination and which may have value in direct comparison of samples. The components determined with this technique are shown in Figure 1.

One factor complicating the identification of the type of powder is mixing of single-base and double-base powder in a device. The single-base powder will be contaminated by NG and testing of grains of this powder will erroneously identify it as double-base.

FIGURE 1. HPLC gradient elution of smokeless powder additives with UV detection. Method developed by E.C. Bender.



A large body of literature has been generated on the aging of smokeless powder stabilizers for the purpose of predicting safe propellant shelf lives [6-10]. Much of this research has been on artificially aged propellant, yet some of the most important derivatives are seen in powders stored at ambient temperature, and this is a most fruitful area for comparisons.

The analysis of plasticizers, stabilizers, etc. is of indisputable value for performing forensic comparisons, but further study is needed to determine their identification value. The additives may be indicative of a particular producer or product when routinely used by the producer; however, they may arise as a result of reworking old lots of powder. With the limited current availability of surplus powders, chemical composition differences may be more significant for identification than previously. Consistent qualitative compositional differences discriminate similar powders, but the significance of each component must be understood to definitively identify smokeless powders.

NITROCELLULOSE: PERCENT NITRATION AND MOLECULAR WEIGHT DISTRIBUTION

Certain propellants, particularly those marketed by Scot Powder Co. of Ohio, advertise the advantage of their nitrocotton based powders. It is well known that cotton linters nitrate to a narrower range than wood pulp. Kohlbeck [11] described differentiation of different levels of cellulose nitration by polarized light microscopy. Baker et al [12] also showed that the biological source of the cellulose has a significant effect on other physical properties of the nitrocellulose.

Nitrocellulose molecular weight changes with time as it degrades. The analysis of cellulose nitrate by gel permeation chromatography for comparisons is a subject of continuing work in our laboratory. Carignan and Turngren [13] demonstrated that the polymer was effected by thermal degradation and this may limit the technique when particles are obviously blast damaged.

PROPRIETARY COATINGS

Another area of current investigation is coating materials. Preliminary investigations suggest that different surface coatings, other than plasticizers, deterrents, flash suppressors, etc. may permit the discrimination of a powder made by one producer from a highly similar powder made by another.

GRAPHITE

The graphite used for glazing may also be useful in discrimination of ball-type powders. In domestic production, synthetic graphite is used on some propellants, whereas one imported product uses natural graphite. Natural graphites contain entrained clays which vary with the geographical origin of the mineral. Synthetic graphite is a carbon product which has been baked to alter the crystallographic structure; the impurity content is low. An initial survey of minor elements in the graphite by SEM/EDX has been made and some differences observed but additional study is required to assess the significance of the observed variations.

PARTIALLY BURNED PARTICLES

When smokeless powder is recovered from post-blast debris, partially burned particles are frequently recovered. Andrasko [14] found that the composition of partially burned particles left

after firing a gun, showed good correlation to the original powder, with the exception of dibutylphthalate, a common surface coating. According to manufacturer information, the coating is always applied before the glazing step, so if the graphite layer is intact the deterrent coatings will be present. In the case where the graphite is lost with the blast, it is important to realize which ingredients are incorporated into the nitrocellulose lacquer and which were applied as surface coatings. Stine [15], analyzed partially burned particles of single base smokeless powder and found that the stabilizer (DPA) levels remained the same or decreased slightly. Increased levels of degradation products (2-nitroDPA and 4-nitroDPA) were also noted when compared with unburned propellant.

Appearance

Several brands incorporate identifier dots; particles colored with dye to indicate the product type and brand. These too change with time since the colors vary from batch-to-batch. As an example, Hercules Inc. markets Hercules Green Dot[®], originally a perforated disc. In 1970 or 1971 the perforation was removed and the particle diameter was increased by approximately 0.15mm. One phenomenon noticed in our exemplar collection was the tendency for the color of the blue dots to shift to a greenish color with the formation of yellow stabilizer derivatives. In 1980 or so, a filler, TiO_2 , was added improve visibility of the indicator dots, and the dyes were changed so that newer dots have a distinctly different appearance from those used earlier. Changes such as these, that date a powder, are important for providing investigative leads and understanding the significance of comparisons.

Color of the grain may also be useful in discrimination of morphologically similar powders. Scot Powder Co. has recently added SCOT 453™ to its product line, this spherical propellant is manufactured in Czechoslovakia. The particles are quite small and undistinguished in appearance, but when a particle is cut open, the dough is extremely porous and its internal color is a stark white rather than the expected amber, green, blue or black (from carbon black). This unusual feature may be unique to this powder and valuable for establishing its identity.

Implications of Manufacturing and Marketing Practices on Brand Identification

It must be recognized that the primary specification for smokeless powder is ballistic performance, not chemical composition. Producers or vendors blend batches or sub-lots of powder to obtain the desired ballistic characteristics. As a result, lot-to-lot variation will be observed even for the same product.

MANUFACTURING

Over time, physical changes may be made by the original producer or vendor. Examples include DuPont (currently IMR) 700-X whose morphology changed from a perforated to a non-perforated disc in the early 1980s, and Hodgdon H-4227, whose length and diameter differed in the 1987

product as compared to that offered in 1983 [16,17].

European practice often considers powders containing less than 12% NG as single-base. For example, Norma 201, made in Sweden, and represented as single base, is reported to contain 5% NG [18]. In a laboratory examination, this level of NG is readily detectable and for the purposes of searching the database must be considered to be double-base.

In post-blast debris, only one or two particles may be recovered. Chemical analysis should be used cautiously for identification in this instance. The concern is attributable to a common industry practice where sub-lots are blended. Certain basic recipes are manufactured and tested ballistically, the performance determining which sublots will be blended into the finished lot.

MARKETING

The producer or vendor of the powder may also be identifiable. In this context, the producer is the actual manufacturer of the powder, who may or may not sell it under his own name (or brand). In the United States, there have long been vendors who sell purchased powder: surplus, domestic or imported, under their brand name. A major supplier of name-brand reloading, or canister powder, Hodgdon, neither produces nor reworks powder. They buy and blend military surplus or powder produced by major commercial manufacturers and repackage it under their brand-name and designation.

In a number of instances, the same propellant is offered under two or more brand names. Hodgdon Powder Co. markets Ball powder manufactured by Olin. The same propellants are marketed by Winchester Western (Olin) and under another designation by Hodgdon. The manufacturer's designations have no direct correlations to Hodgdon nomenclature. One Olin powder may be marketed by Hodgdon as H380, H414, or H450, depending on the results of ballistic testing of the lot.

The morphology of another Hodgdon powder, H-450 has also undergone a cycle of change. The original lot was an Olin produced Ball powder, probably purchased as military surplus, and marketed during the early to mid 50s. When this supply was exhausted, powder was purchased from Olin for H-450; however, this new product was a Flattened Ball. The powder was unavailable during the much of the 1970s and 80s. Since 1988, H-450 is once again a Ball-type, purchased as military surplus.

When Scot Powder Co. introduced Royal Scot® in 1988, the powder was a Disc with an orange identifier, recently the name was changed to Royal Scot D™, reflecting a change in manufacturer and the removal of the identifiers.

For reloading purposes, smokeless powders are often designated as equivalent in performance to a well known powder, this is common with IMR type powders. Table 1 illustrates the number of powders on the market with the 4350 designation. The product was originally manufactured by DuPont with Hodgdon selling surplus product. The DuPont product was manufactured by Expro of Canada beginning in 1978. Since 1988, the Expro powder has been marketed by IMR Powder Co. During this time, the surplus market dried up, and Hodgdon turned to ICI of Scotland to produce "4350". Since 1989, Hodgdon has also been marketing H4350 manufactured by ADI of Australia. In the last two years, Accurate Arms Company began marketing a product called 4350 which is manufactured by Israeli Military Industries (IMI) in Israel. Table 1 shows the dimensions

for different lots of powder by these manufacturers. As described in the paper by Selavka et al. [1], when an unknown powder is measured and searched against the database, it is compared to the average for each type of powder plus or minus two standard deviations from the mean.

Analysis of these powders shows that H4350 manufactured in Scotland contains DPA and Methyl Centralite, while H4350 made in Australia, IMR 4350, and Accurate 4350 contain DPA and DNT.

TABLE 1. A comparison of measurements of different brands and lots of powder marketed as ballistically comparable to IMR 4350. Measurements are in millimeters.

Product Designation	Where Made	Year Made	LENGTH mean	LENGTH S(x)	DIAM mean	DIAM S(x)	WEB mean	WEB S(x)
DuPont IMR 4350	USA	1978	2.12	0.06	1.02	0.03	0.45	0.04
DuPont IMR 4350	USA	1977	2.13	0.11	0.95	0.03	0.40	0.02
DuPont IMR 4350	USA	1979	2.14	0.06	0.99	0.03	0.42	0.01
IMR IMR 4350	Canada	1991	2.22	0.09	0.96	0.03	0.41	0.02
IMR IMR 4350	Canada	1992	2.13	0.08	0.98	0.03	0.40	0.02
Accurate 4350	Israel	1991	2.19	0.10	0.99	0.06	0.49	0.03
Hodgdon H4350	Scotland	1985	2.05	0.12	0.93	0.03	0.38	0.05
Hodgdon H4350	Scotland	1988	2.15	0.14	0.93	0.06	0.37	0.04
Hodgdon H4350 *	Australia	1989	1.95	0.07	1.02	0.03	0.44	0.02

* The perforation is sealed on most particles.

Database Scope and Limitations

From the particles recovered after a pipe bombing, the laboratory may be able to determine the brand-name and designation under which a particular powder was sold, as for example, Hercules Red Dot or Accurate 8700, to uniquely identify the product. In other cases, the best information that can be developed is the manufacturer's designation and a list of potential brand names. Partial or fragmentary grains or mixed powders pose additional problems in identification. When powder recovered from a device and from a suspect or from several separate incidents are submitted to the lab, testing may be conducted to compare the samples. The goal of this examination is to establish a link between the samples to show common origin, useful as evidence in the prosecution of the bomber or even to demonstrate that the samples are unrelated.

As indicated, identification of the producer and/or brand name of a smokeless powder is a prime laboratory objective in the examination of physical evidence in pipe bombing incidents. A number of factors beyond the control of the analyst complicate this identification and limit the laboratory's

reporting of definitive results. Marketing factors constrain brand identification of canistered smokeless powder. When the powder used has been removed from ammunition, the sheer numbers of cartridge and powder types, as well as blending of powders by the ammunition producer, poses almost insurmountable problems. For this reason, we have restricted our identification efforts to those powders sold in bulk for reloading purposes. Even with this restriction, since canisters are the easiest way to obtain enough powder for a pipe bomb, the database has been used routinely and successfully in our laboratory examination. Mixed powders, however, are highly useful for comparative purposes because the blending may produce a distinctive product. Because they do not produce all types of powder, major producers may sell, under their brand, imported products to fill out their product line. They may also buy and rework surplus military powders introducing components, detectable by chemical analysis, not normally present in their products.

Conclusion

Using a computer searchable database combining information from morphology, appearance and chemical testing with additional information on the product, we have had good success in uniquely identifying or limiting to a small number of potential candidates, canister smokeless powders encountered in the examination of evidence from pipe bombs. Regardless of the approach used; however, the prime requirement for success in identification of the producer, brand and designation of reloading smokeless powders is the availability of an extensive reference collection. Access to references (such as Handloader) and industry contact are also vital. Because of constant change in the powders available to the public, this collection must be constantly updated. Newly available powders must be acquired immediately, examined and their characteristics added to the database. In addition, new samples of common powders must be obtained on a regular basis to identify changes, made without fanfare, which could either make them unidentifiable with the existing system or lead to an erroneous identification or elimination. Identification of smokeless powders is a valuable tool in the investigation of pipe bombings but, without continual revision of the reference data, this tool will quickly lose its edge.

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APPLICATIONS OF ION CHROMATOGRAPHY FOR DETERMINATION AND IDENTIFICATION OF CHLORATE, NITRITE AND NITRATE IN EXPLOSIVES AND EXPLOSIVE RESIDUES

Sara Abramovich-Bar, Yair Bamberger, Mark Ravreby and Shlomo Levy. Division of Identification and Forensic Science, National Police Headquarters, Jerusalem, Israel.

Abstract

Applications of ion chromatography for determination and identification of chlorate, nitrite and nitrate in various combinations and ratios in actual cases of explosives and explosive residues were investigated. The system consisted of a Dionex Ionpac AS9 column combined with a suppressor column and a conductivity detector. Using a 25 μ l sample size, linear calibration graphs were obtained in the range of 10-100 ppm for nitrite, nitrate and chlorate. Chlorate or nitrate identification in post explosion residues based on spot tests and an infrared spectrum often do not give satisfactory results. In some cases ion chromatography can be used to replace an unsatisfactory infrared spectrum increasing the confidence in the results and increasing the detection limits. Nitrite in post explosion residues is a decomposition product and not a component of the explosive mixture per se. In general the infrared spectrum is of poor quality and the Griess test combined with ion chromatography satisfy the criteria of two independent test results. Post explosion residues containing nitrite and nitrate present special problems. Identification based on spot tests (Griess test with and without zinc reduction) and infrared spectra are frequently problematic partially due to unknown interferences in the nitrate spot test and a high ratio of nitrite to nitrate. Ion chromatography can be very useful to overcome many of these problems and give an indication as to whether the problem is due to an unknown interference or a high nitrite: nitrate ratio.

Introduction

At the Israel National Police analytical laboratories the three major anions of interest associated with explosives and post explosion residues are chlorate, nitrate and nitrite ions. In our laboratory it is considered necessary to have positive results from two independent

tests for positive identification of these anions. Prior to purchasing an ion chromatography system our methods of analysis consisted primarily of spot tests and infrared spectrophotometry. Quite frequently the results of the spot tests or the infrared spectra were inconclusive or unsatisfactory. In an effort to enhance our analytical capabilities, improvements were made on some of the spot tests and in early 1991 ion chromatography analysis methods were introduced for this purpose.

Ion chromatography first appeared in the literature in an article by Small, Stevens and Baumen in 1975 (1) followed by several articles on applications to explosives and explosive residues (2-6). In this paper numerous applications of ion chromatography to actual casework are discussed.

Experimental

SPOT TESTS

Modified Griess Test - A solution consisting of 40 grams of sulfanilamide and 50 ml of concentrated phosphoric acid is diluted to a volume of 500 ml with distilled water. A second solution consisting of 2.75 grams of N-1-Naphthylenediamine dihydrochloride and 50 ml of concentrated phosphoric acid is diluted to a volume of 500 ml with distilled water. Prior to use the two solutions are mixed in a 1:1 ratio and a drop of the mixed solution added to the material to be tested on a spot plate. The mixed solution is unstable and never stored for more than a few days.

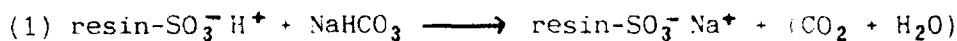
Chlorate Spot Test - A drop of 5% aqueous aniline sulfate and a drop of concentrated sulfuric acid are placed on a spot plate to the material to be tested.

Azide Modification - To an aqueous solution of the material to be tested a few grains of sodium azide are added and a drop of concentrated sulfuric acid added. The solution is heated to near boiling for approximately five minutes. A drop of the solution is then tested with the modified Griess reagent to insure that the nitrite ion has been completely removed, followed by zinc reduction.

Instrumentation

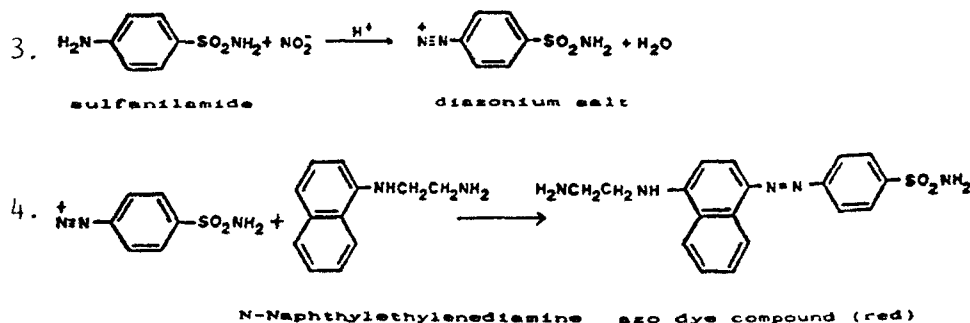
The infrared spectra were obtained using a Laser Precision Analytical RFX-30 FTIR with a DTGS detector. An Elgastat VHQ water purifier unit was used to obtain water with a resistivity of 18 Megohm-cm for the ion chromatography experiments. A Dionex series 4500i Ion Chromatography System with a Dionex Ionpac AS9 separator column followed by a suppressor column and a conductivity detector were used.

The eluent consists of a 0.75 mM NaHCO_3 and 2.0 mM Na_2CO_3 buffer system. The suppressor column contains a strongly acidic cation exchange resin in the hydrogen form which converts the highly conductive sodium bicarbonate into the weakly dissociated carbonic acid. It also converts the anions into their corresponding acids. The net result is to increase the detection sensitivity of the ions via their conductivity. The reactions involved are illustrated below :



Results and Discussion

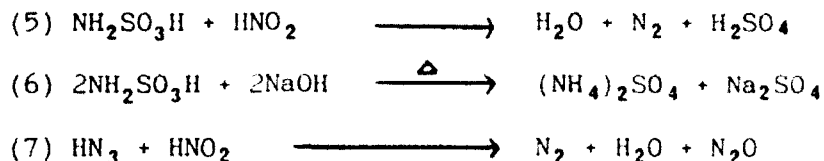
Before discussing several cases where ion chromatography was useful in confirming the identification of various anions, a brief review will be given of the analytical methods we use and some of the more recent modifications made in the spot tests. The spot tests used for nitrate and nitrite ion are a modified Griess test with and without zinc reduction using sulfanilamide and N-1-Naphthylethylenediamine in 10% phosphoric acid (7). The diazotization and coupling reactions are as follows :



The spot test for chlorate is based on the reaction with 5% aniline sulfate and sulfuric acid which gives a blue-purple color. This spot test also gives a positive reaction with bromate ion.

In concentrated solutions containing nitrite and nitrate ions or in solutions containing a high nitrite : nitrate ratio it can be difficult to visually observe the increased color intensity due to nitrate ion using the Griess reaction and zinc reduction. Visually it is far easier to detect a transition from a colorless solution to a pink color than a red solution to a more intensely red solution. To achieve this involves either separation of the nitrite ion from the nitrate ion or decomposition of the nitrite ion. In actual cases we had very limited success separating the nitrite ion from nitrate ion based on phase transfer methods (8).

Two standard methods for decomposing nitrite ion involve sulfamic acid or an azide (9). The principle reactions are given below :



Using sulfamic acid no problems were encountered in readily decomposing the nitrite ion (reaction 5). However, we did encounter problems trying to dispose of the excess sulfamic acid (reaction 6) and in tests where the solutions were heated to near boiling for fifteen minutes under alkaline conditions, excess sulfamic acid still remained in solution. As a result the azide reaction was tried (reaction 7). Using sodium azide under acidic conditions nitrite ion was readily decomposed and by heating to near boiling the excess azide was removed. This modification was applied to cases which were problematic for nitrate identification using the Griess reaction with zinc reduction.

A sample chromatogram is illustrated in Figure 1 showing some anions of interest. The retention time in minutes is given after each peak. There is excellent separation of chlorate ion from nitrate ion, which was a problem with many other columns. Bromate ion, which is not illustrated, is also separated from chlorate ion with a retention time slightly less than that of chloride ion and not completely resolved from it. This does not present any particular problem since what is usually of interest is the presence or absence of chlorate ion, and in actual casework retention time is confirmed by spiking with the appropriate anion.

Calibration graphs of nitrite, nitrate and chlorate ions are illustrated in Figure 2. The three anions are linear in the range of 10-100 ppm. Both chlorate and nitrate ions are linear up to 200 ppm although nitrite ion exhibits non linearity at 200 ppm. Below 10 ppm both chlorate and nitrate ions exhibit non linearity while nitrite ion is essentially linear to the origin. No attempt was made to determine absolute lower detection limits although it is clear that these limits are much less than one ppm.

The following example and cases illustrate typical problems associated with chlorate ion. In the first example a synthetic mixture of sucrose and match heads, containing primarily potassium chlorate, was prepared. With modern FTIR techniques and spectral subtraction, sucrose could be spectrally subtracted from the mixture resulting in a satisfactory spectrum of potassium chlorate. In the synthetic mixture prepared a large excess of sucrose was deliberately taken and the infrared spectrum compared with that of standard potassium chlorate (Figure 3). The presence of potassium chlorate is not indicated in the infrared spectrum of the synthetic mixture and the best spectral subtraction of sucrose from the synthetic mixture (Figure 4) is obviously unsatisfactory. However, a combination of the two more

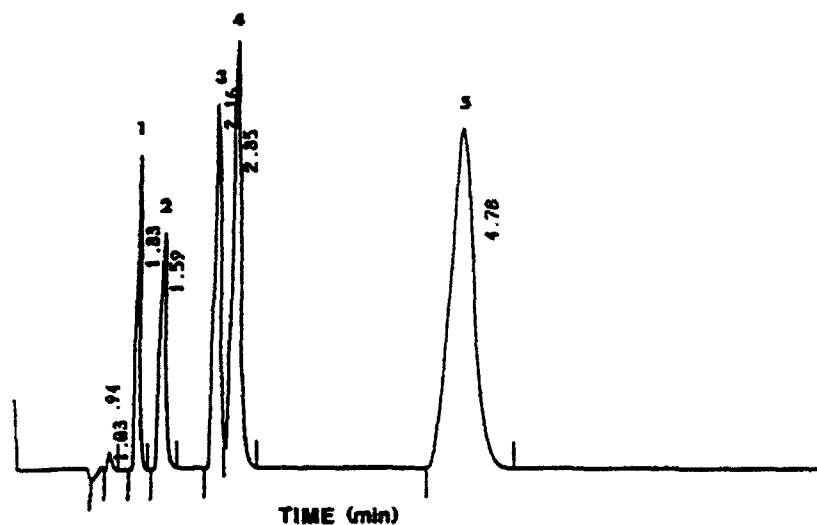


Figure 1. A sample ion chromatogram showing some anions of interest :
 (1) Cl^- 5ppm, (2) NO_2^- 10ppm, (3) ClO_3^- 25 ppm, (4) NO_3^- 25ppm,
 (5) SO_4^{2-} 30ppm.

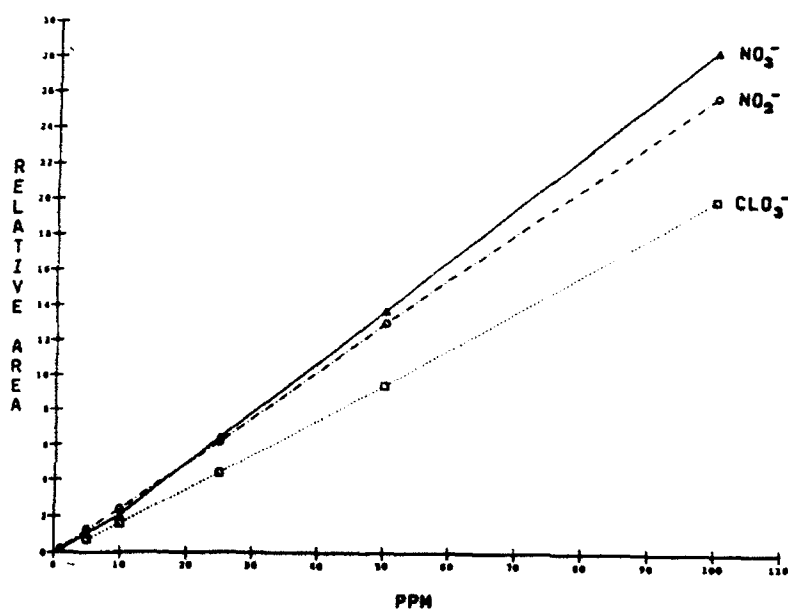


Figure 2. Calibration curves for nitrate, nitrite and chlorate.

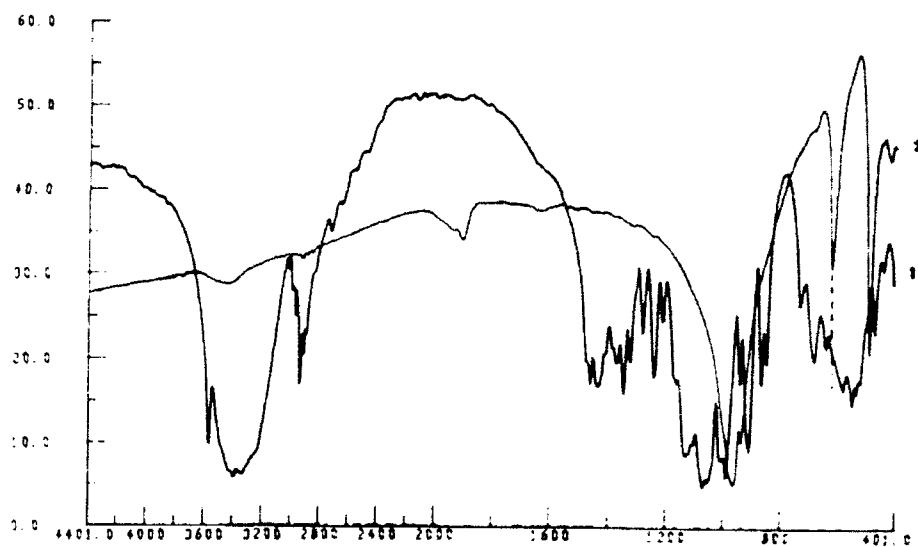


Figure 3. Infrared spectra of : (1) a synthetic mixture of sucrose and match heads, (2) standard KClO_3 .

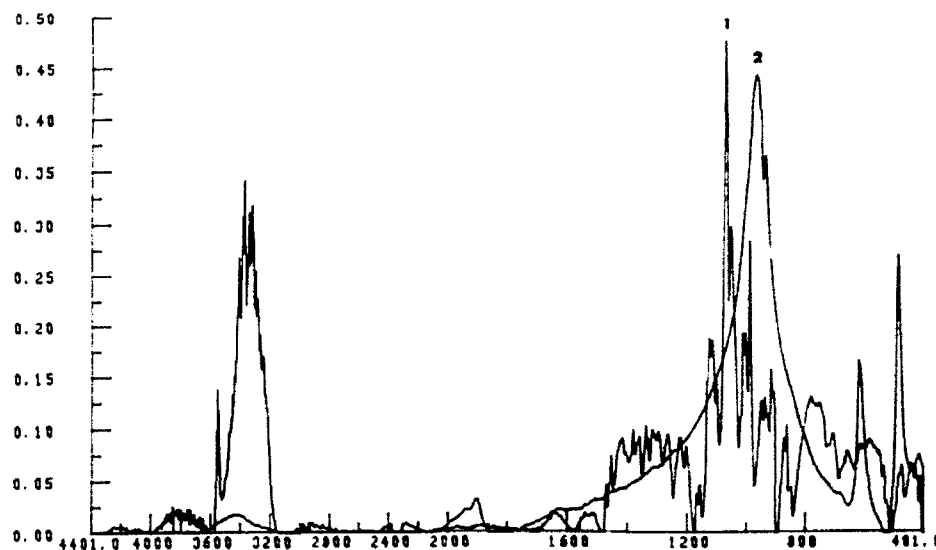


Figure 4. Infrared spectra of : (1) spectral subtraction of sucrose from a synthetic mixture of sucrose and match heads, (2) standard KClO_3 .

sensitive tests, namely a positive spot test and positive results from the ion chromatography (Figure 5) were considered adequate for identification of the chlorate ion. Determination of the chlorate ion by ion chromatography gave results of 1.9% chlorate ion or 2.9% calculated as potassium chlorate, which explains the difficulties encountered in the spectral subtraction.

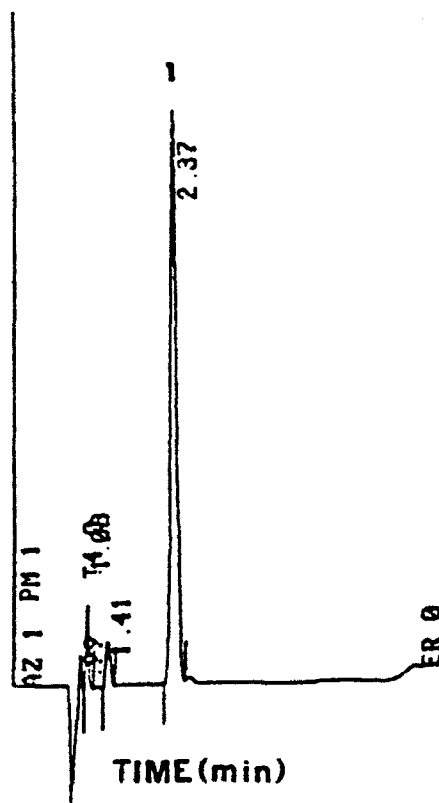


Figure 5. Ion chromatogram of a mixture of sucrose and match heads :
(1) ClO_3^- .

Table 1 summarizes the results of this example and several cases. Case 1 is material before an explosion from a home made device which also contained nitrate ion as confirmed by all three tests. The spot test for chlorate ion was inconclusive and the infrared spectrum was poor. The negative results for chlorate ion by ion chromatography confirmed its absence. Case 2 and case 3 are post explosion residues and similar. In both cases the spot test for chlorate ion was positive but the infrared spectra were poor or unsatisfactory. In the infrared spectrum from case 3 (Figure 6) there are indications of the presence of chlorate ion but the quality of the spectrum is not sufficient to confirm its presence. In both cases the positive results by ion chromatography confirmed the identification of chlorate ion with case 3 illustrated in Figure 7.

TABLE 1. Test results for chlorate ion

SPOT TEST	IR	ION CHROMATOGRAPHY	
+	POOR	1.9% CHLORATE 2.9% AS POTASSIUM CHLORATE	MATCH HEADS + SUCROSE
ClO ₃ ⁻ ? NO ₃ ⁻ +	ClO ₃ ⁻ POOR NO ₃ ⁻ GOOD	ClO ₃ ⁻ — NO ₃ ⁻ +	CASE 1
+	POOR	+	CASE 2
+	UNSATISFACTORY	+	CASE 3

Table 2 summarizes the test results of several cases containing nitrate and nitrite in post explosion residues. A few general trends are readily obvious. The Griess test for nitrite ion was never a serious problem and in all of the cases illustrated gave positive results. However the Griess test for nitrate ion was problematic in most of these cases. From the results of the ion chromatography tests it becomes apparent that in all of these cases the nitrate ion concentration is greater than that of the nitrite ion concentration. As a result in cases where the Griess test for nitrate ion was problematic we could exclude the possibility that the problem was due to a high nitrite ion concentration and a low nitrate ion concentration and the difficulty of distinguishing between a darker red solution from an already red solution.

TABLE 2. Test results for nitrate and nitrite

SPOT TESTS				IR		ION CHROMATOGRAPHY			CASE
AZIDE+GRIESS TEST		GRIESS TEST							
+ Zn		+ Zn		NO ₃ ⁻	NO ₂ ⁻	NO ₃ ⁻ NO ₂ ⁻	PPM NO ₃ ⁻	PPM NO ₂ ⁻	
NO ₃ ⁻	NO ₂ ⁻	NO ₃ ⁻	NO ₂ ⁻	NO ₃ ⁻	NO ₂ ⁻	NO ₃ ⁻	NO ₂ ⁻	NO ₃ ⁻	
+	-	? color too intense	+	GOOD	FAIR	11	16	1.5	4
+	-	? intensity does not increase, fades	+	GOOD	FAIR	3	8.5	3	5
+	-	? color increase then fades	+	POOR	POOR	6	12	1.75	6
		+	+	POOR	POOR	1.5	6.5	4	7
		? no increased intensity	+	GOOD	VERY WEAK	3	19	6.5	8

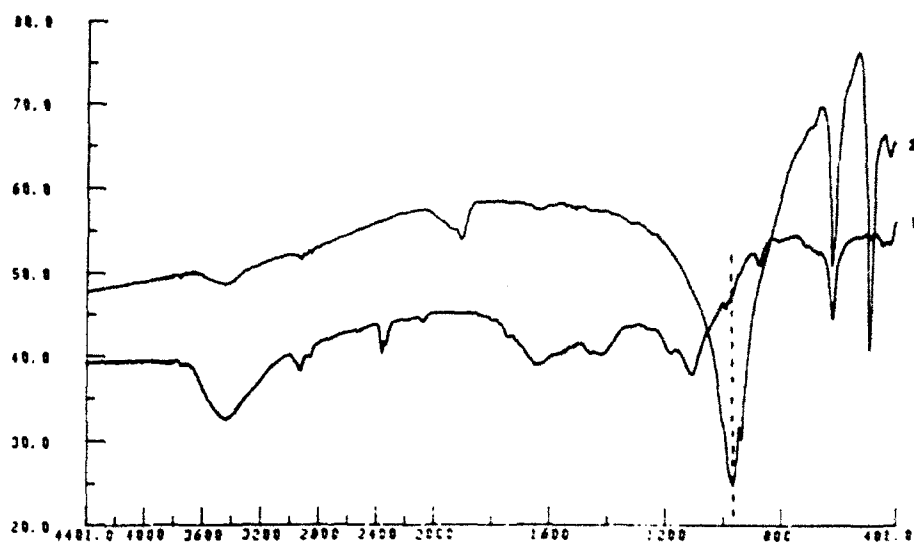


Figure 6. Infrared spectra of : (1) case 3, (2) standard KClO_3 .

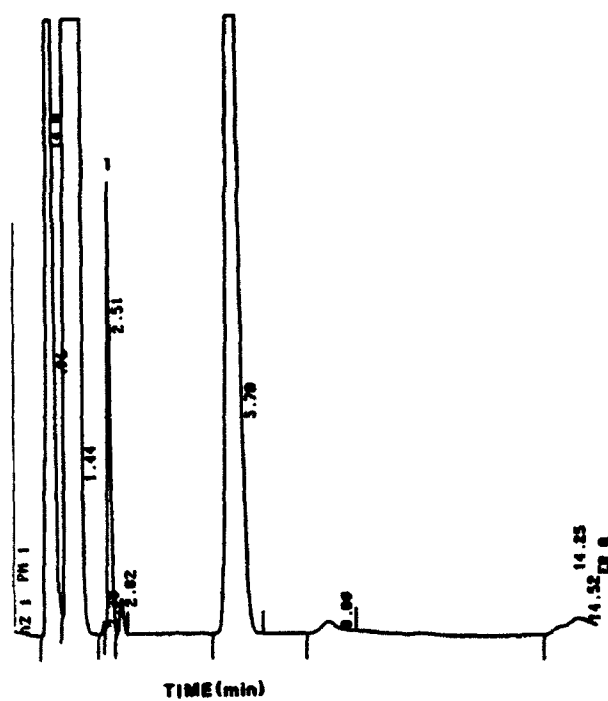


Figure 7. Ion chromatogram of case 3 : (1) ClO_3^- .

In case 4 the infrared spectrum for nitrate ion is very good and the infrared spectrum for nitrite ion is fair (Figure 8). The Griess test for nitrate ion was problematic but with the azide reaction gave satisfactory results. The Griess test for nitrite ion was satisfactory and the ion chromatograph results confirmed its presence. Case 5 is fairly similar with a good infrared spectrum for nitrate ion and a fair infrared spectrum for nitrite ion. The Griess test for nitrate ion was unsatisfactory and not only was there no increase in the color intensity but to the contrary the color present faded. With the azide reaction and the Griess test the presence of nitrate ion was confirmed. Nitrite ion was confirmed by ion chromatography.

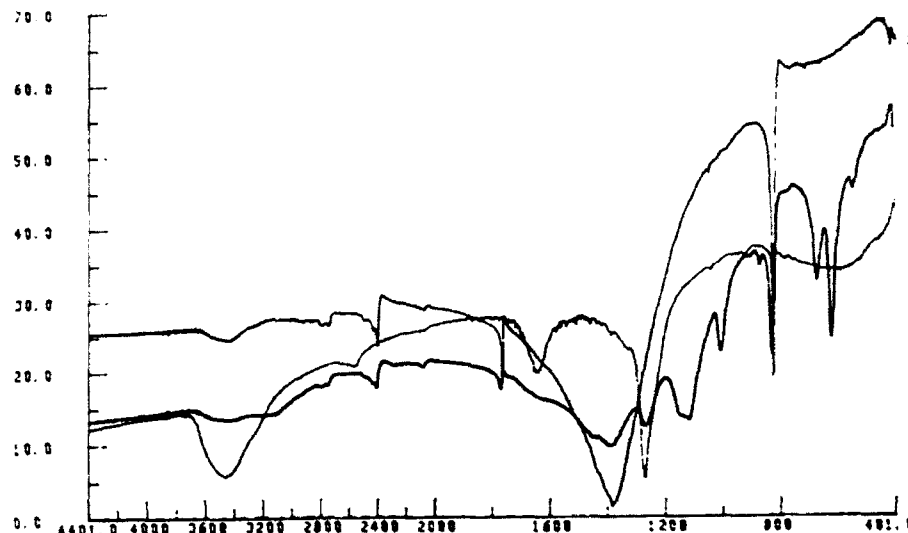


Figure 8. Infrared spectra of : (1) case 4, (2) standard NaNO_2 , (3) standard KNO_3 .

In case 6 the infrared spectrum was poor for both nitrate and nitrite ions. The Griess test for nitrate ion was inconclusive with an increase in color intensity followed by the color fading. The azide reaction followed by the Griess test gave satisfactory results. The Griess test for nitrite ion was satisfactory and the ion chromatography results confirmed the presence of both nitrate ion and nitrite ion (Figure 9). In case 7 the infrared spectrum was poor for both nitrate and nitrite ions (Figure 10), the Griess test was satisfactory for both nitrate and nitrite ions and ion chromatography confirmed the presence of both ions (Figure 11).

The analyses on case 8 were performed before we had perfected the azide modification. In addition to the results summarized in table 2 the spot test for chlorate ion was positive but the infrared spectrum was poor. The presence of all three anions - chlorate, nitrate and nitrite was confirmed by ion chromatography as illustrated in Figure 12.

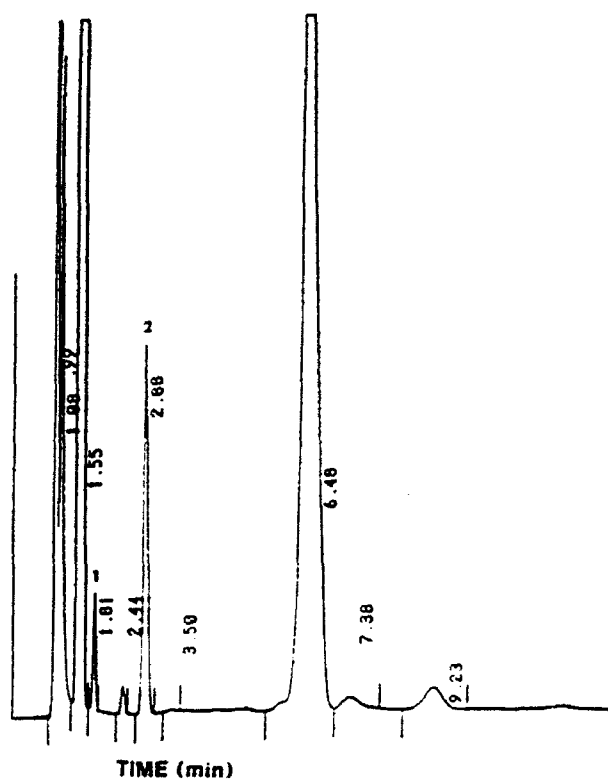


Figure 9. Ion chromatogram of case 6 : (1) NO_2^- , (2) NO_3^- .

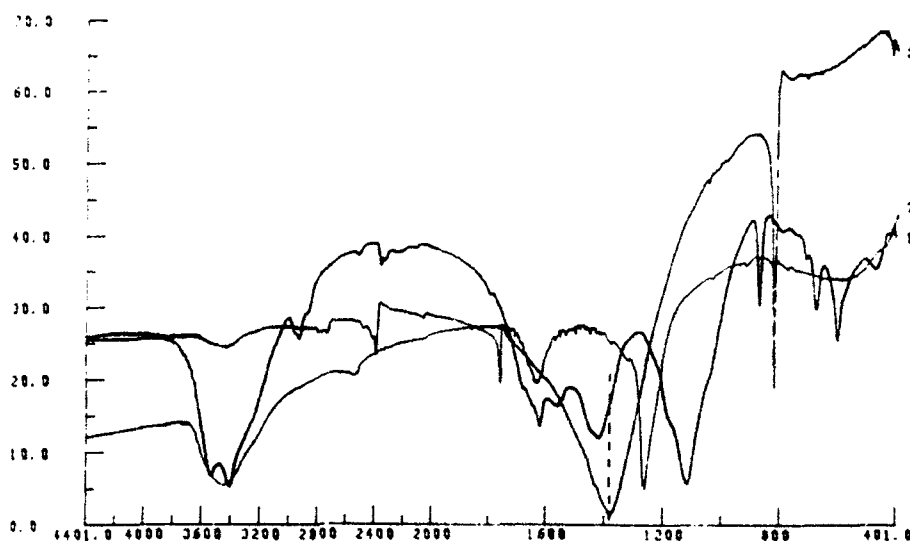


Figure 10. Infrared spectra of : (1) case 7, (2) standard NaNO_2 , (3) standard KNO_3 .

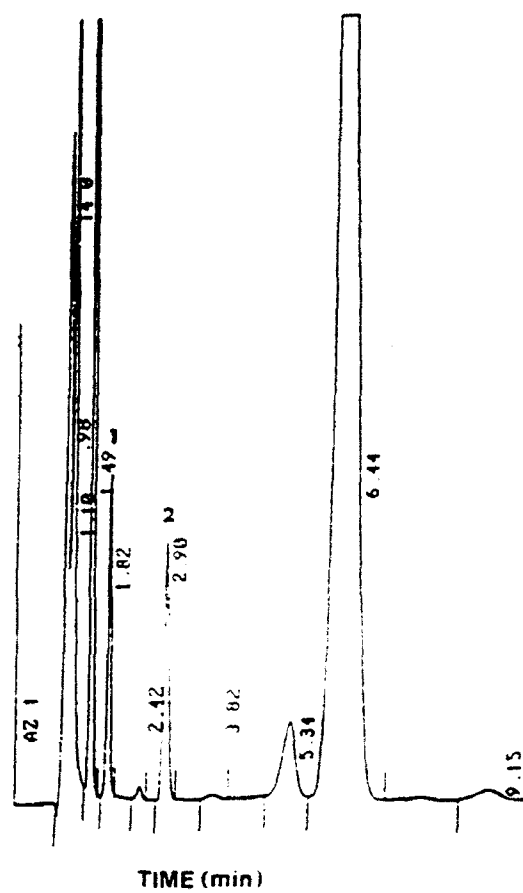


Figure 11. Ion chromatogram of case 7 : (1) NO_2^- , 2) NO_3^- .

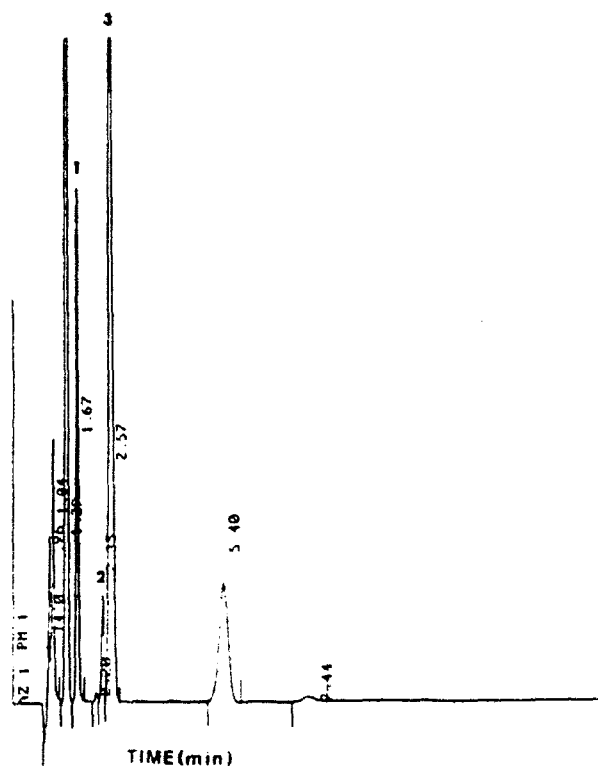


Figure 12. Ion chromatogram of case 8 : (1) NO_2^- , (2) ClO_3^- , (3) NO_3^- .

Conclusions

Ion chromatography is a very useful method to confirm the presence or absence of anions associated with explosives and post explosion residues, specifically chlorate, nitrate and nitrite ions. As illustrated with several cases it can frequently be used as an alternative method to replace poor or inconclusive results from spot tests or infrared spectra supplying the necessary test to satisfy our criteria of two independent tests for positive identification of these anions.

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SAMPLE PREPARATION BY SUPERCRITICAL FLUID EXTRACTION IN EXPLOSIVES TRACE ANALYSIS

P. KOLLA
Bundeskriminalamt
Fachbereich KT 23
Postfach 1820
6200 Wiesbaden
Germany

H. ENGELHARDT, J. ZAPP
University of Saarland
6600 Saarbrücken
Germany

ABSTRACT. Supercritical fluid extraction is applied to the trace analysis of organic nitro-explosives. The method is adopted on soil, swabs and dust. The recovery at sufficient pressure is usually higher than 60% with pure CO₂ as extraction reagent without addition of modifiers. The CO₂ can easily be removed by evaporation. The recovery increases with decreasing polarity of the molecule, corresponding to the elution behaviour in reversed phase liquid chromatography. The higher the carbon content of the matrix, the less is the recovery of the explosives. The analysis of real samples from experimental blasts shows, that the explosive residues are found in swabs from metal plates near the center of the explosion.

INTRODUCTION

Extraction with supercritical carbon dioxide (SFE) has been used widely in the analysis of plant constituents for drug analysis [1-4], especially with subsequent coupling to thin-layer chromatography for extract monitoring. SFE is becoming more and more applied to the great variety of analytical problems e.g. to the trace analysis in soils [5] as well as to the analysis of additives in polymers [6]. SFE may be superior to classical liquid extraction for speed, completeness and selectivity. It is extremely easy to separate the extraction reagent, the CO₂, from the extracted solute. Carbon-dioxide is able to dissolve substances, that are soluble in non-polar to medium-polar solvents, usually in the polarity range between aliphatic hydrocarbons and dichloromethane. The solvent strength of CO₂ can be increased by increasing pressure and decreasing temperature. In addition it is possible to extend the polarity range of the solvent power in mixing a polar modifier such as acetone or methanol to the CO₂. The extracts from SFE may be analyzed by chromatographic methods without further preparation.

It is reasonable to use SFE also in the trace analysis of explosives [7]. The extraction with moderate polarity and low temperature is a preferred feature for the sample preparation of explosives. The amount of the substances, that are extracted together with the explosives is limited to those with similar polarity. SFE can be applied to all porous supports such as soil, dust or swabs. In this paper the application of SFE to the trace analysis of explosives in combination with selective chromatographic detection is demonstrated.

EXPERIMENTAL

A Suprex SFE/50 (Suprex, Pittsburg, USA) equipped with two multipleport valves was used. Standard HPLC column tubes (2, 4 or 7 mm i.d., length 5, 10 or 25 cm) were installed as extraction vessels. The extractors were packed dry with the matrix.

The extraction was usually performed in the continuous mode. The extract was allowed to expand via a deactivated fused-silica restrictor (10 μm or 20 μm i.d.) directly into a volumetric flask. To prevent sample loss, the restrictor end was immersed in acetone or the HPLC eluent. The flask was usually filled to one third of its total volume. Before injection it was necessary to degas the solution by sonication.

CHROMATOGRAPHY

The analysis of the SFE extracts was performed by HPLC or GC-TEA. HPLC was combined of a Waters 590 pump, Rheodyne 7125 sampling valve with 20 μl loop and Waters 484 UV detector. HPLC columns were RP18 columns from Bischoff, Leonberg, Germany. The gas chromatograph was a Varian 3400 with split/splitless injection coupled to a thermal energy analyzer (TEA) from Thermedics. The TEA was modified as described in [8] in order to make it compatible to capillary GC and to enhance the sensitivity.

RESULTS AND DISCUSSION

The assumption for a sample preparation to be successfully applied in explosives trace analysis is a complete transfer of all explosives into a solution suited for chromatographic analysis. That cannot be managed in one single step for inorganic and organic explosives simultaneously. A separation into classes of explosives is necessary. In the general search for traces of an unknown explosive, the preparation and analysis follows two different ways. Organic nitro-compounds are extracted with a polar solvent such as acetone, the solvent is evaporated and liquid partition or solid phase extraction is applied to clean the extract and to enrich the explosive trace. Salt-based explosives are extracted with water and the ions are analysed by ion-chromatography [9].

SFE is a method to substitute the organic preparation way. Because of the variability of the solvent strength of CO_2 the right conditions

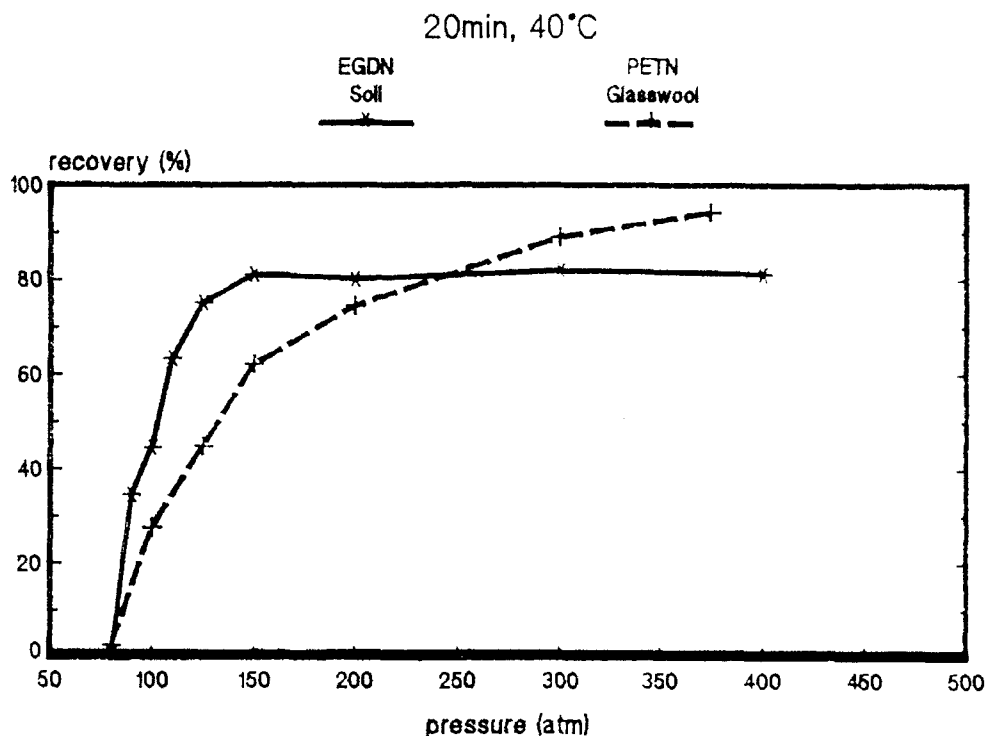


Figure 1: Influence of extraction pressure on explosive recovery

have to be found to extract all the explosives of interest simultaneously with the best recovery and highest selectivity. This was done by the extraction of reference materials such as swabs, spiked with known amounts of explosives. The recovery of each compound was measured at different pressures and different temperatures.

INFLUENCE OF PRESSURE AND TEMPERATURE

If the pressure is increased, the density of the CO_2 rises and thereby it has a higher solvent strength. This effect can be seen in figure 1 with the recovery of PETN from glasswool and EGDN from soil at different pressures. Good recovery i.e. more than 80% is obtained for EGDN at pressures over 150 atm and for PETN at pressures over 250 atm. The temperature selected was 40 °C.

The temperature has no influence on the recovery rate at high pressures (figure 2). Even at subcritical temperatures (23 °C and 30 °C) recoveries around 90 % were found. That is not surprising because at this high pressure the density and thereby the solubility is unaffected by temperature variations. On the other hand at a lower pressure of 100 atm the recovery ranged between 50 % at 50 °C and 25 % at 100 °C. This corresponds to the density variations in this region. Surprising results were obtained by measuring the recovery at increasing temperatures and a fixed density (decreasing the pressures

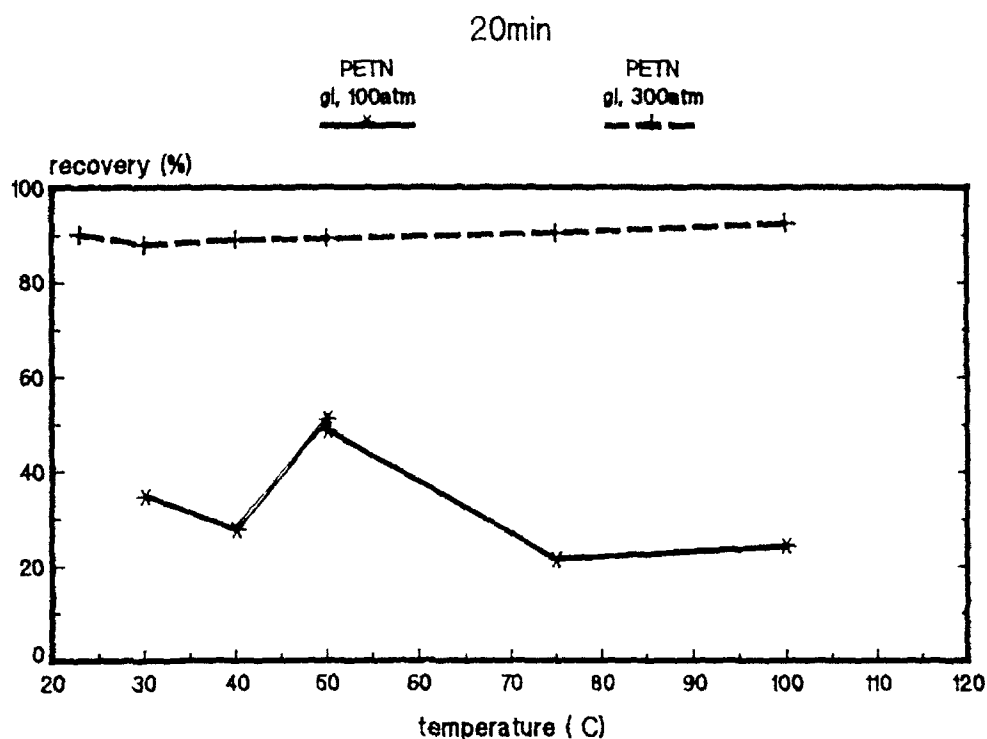


Figure 2: Influence of extraction temperature on explosive recovery at fixed pressure

corresponding to the phase diagram, figure 3). A minimum can be depicted at 80 °C, which can not be explained by theory.

INFLUENCE OF CHEMICAL STRUCTURE AND MATRIX

When discussing extraction of a trace not only the chemical nature of the compound has to be considered but also the nature of the supporting surface. The influence of the matrix was studied by spiking soils of different carbon content with PETN and NG. In figure 4 the results of these investigations are listed. The recovery of NG drops to a value of 34.5 % if it is mixed into soil of a high carbon content. The recovery of PETN is less influenced by the carbon content but it can still be observed. If soils with a high humus content have to be tested, it is recommended to work at high pressures and to extract much longer than usual.

The influence of the chemical structure of the explosive is corresponding to the elution behaviour in reversed-phase HPLC. The less polar an explosive, the later it will be eluted from RP columns and the higher its recovery rate in SFE will be (figure 5). This effect is explained by the less solubility of the polar explosives in the supercritical CO₂.

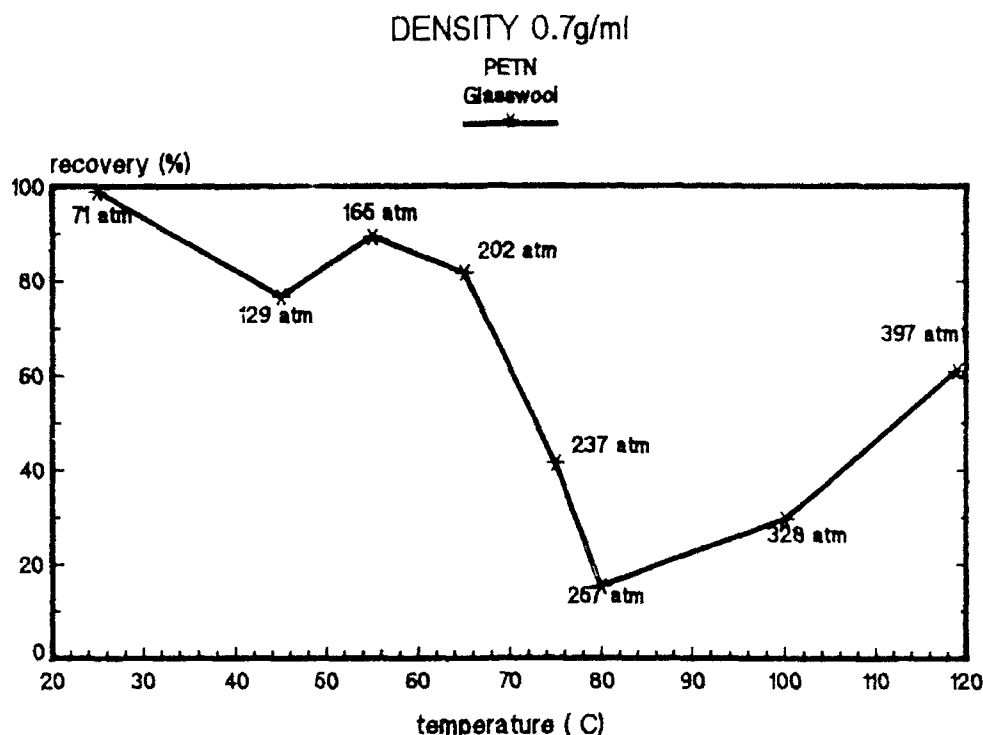


Figure 3: Influence of extraction temperature on explosive recovery at fixed density

ANALYSIS OF EXPLOSIVE RESIDUES AFTER EXPLOSION

The experiments with spiked soil and dust showed that the method can be usefully applied to the extraction of explosives traces. To test the reliability in real cases, experimental blasts were performed. Steel plates were arranged in 1 m and 2.5 m distance from a 500 g explosive charge. After detonation the plates were rubbed with cotton swabs wetted with acetone. The swabs were dried at ambient temperature and extracted by SFE. A pressure gradient was used from 100 atm in 15 min to 250 atm and holding the pressure at 250 atm for 15 min. Analysis was performed with usual HPLC-UV (210 nm). Figure 6 shows the result of a Donarit 1 charge. In figure 6b the analysis of the pure explosive can be seen. The same compounds, EGDN and TNT, can be depicted from the chromatogram in figure 6a showing the SFE of residues collected by rubbing a steel plate in 1 m distance. Figure 7a shows the analysis of a Semtex charge. The HPLC chromatogram of the SFE extract of the swab taken at the plate in 1 m distance obviously shows the problems of explosive trace analysis (figure 7b). Instead of the application of the SFE method there are many unidentified peaks in the UV detection. Unexperienced people may find RDX and PETN in that chromatogram (see arrows). The big amount of PETN in the HPLC-UV

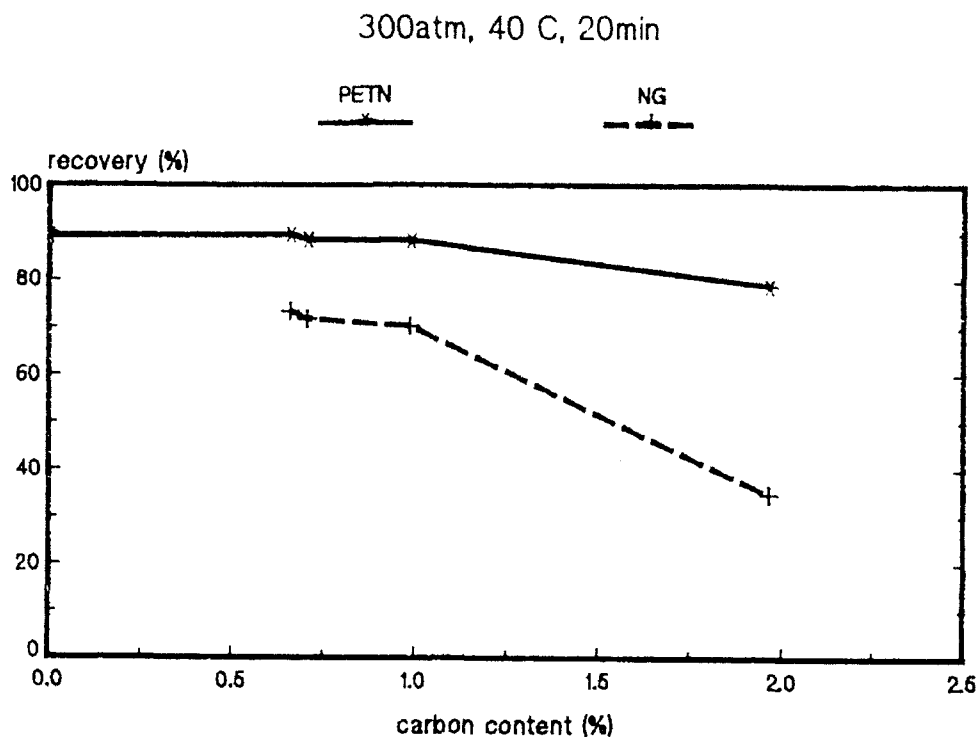


Figure 4: Influence of type of soil on recovery

chromatogram of the swab of 1 m² in 1 m distance gives rise to doubt that the peak is really PETN. If the same sample is injected into the GC-TEA system (figure 8) only a very low amount of PETN is found, which ranges below the sensitivity limit of HPLC-UV. RDX is not found in the extract, but there are peaks of TNT, DNT and NG. These three substances are contaminations of the steel plate from the previous explosion. The steel plate was cleaned with acetone wetted paper before the Semtex experiment, but thereby traces are not totally removed. To avoid such memory effects, the steel plates have to be renewed after each experiment. The GC-TEA result elucidates the necessity of selective detection methods in explosives trace analysis.

Often the task of explosive trace laboratories is the search for explosive contaminations in samples from cars or appartments. Such contaminations are supposed to be caused by any contact with explosives e.g. during the construction or transport of an explosive device. Most of these samples are taken by collecting the dust with a vacuum cleaner. The chromatograms of a SFE extract of the spiked dust from a vacuum cleaner sample show (figure 9), that explosives in the polarity range between RDX and PETN are recovered. The polarity of the CO₂ must be adopted to the range between RDX and PETN in RP liquid chromatography. That is done by a pressure program in the SFE apparatus, or isopycnic with sufficient pressure and temperature values

300atm, 40 C, 20min

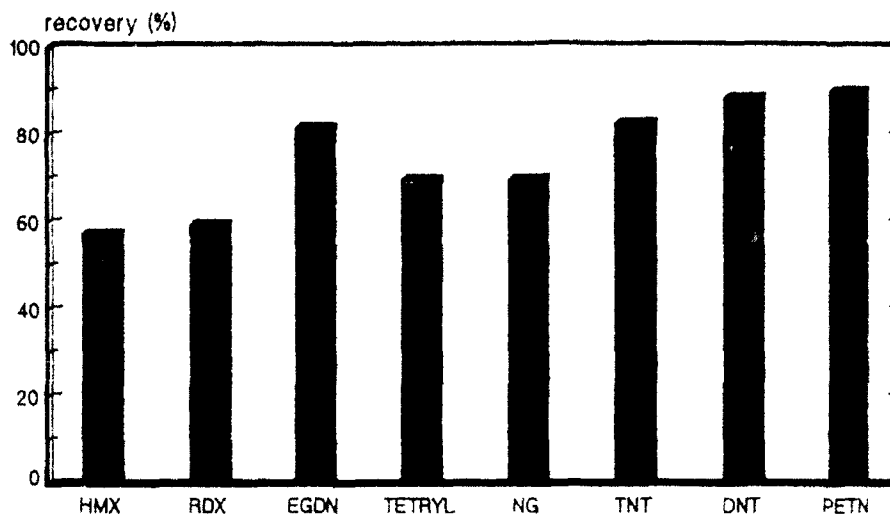


Figure 5: Recovery of explosives from soil

to dissolve RDX. So it is not possible to perform selective extraction for HPLC with UV detection, because the polarity range that is seen in the chromatogram must be chosen to recover the interesting explosives.

CONCLUSION

Supercritical fluid extraction is a useful method for the sample preparation in the trace analysis of organic nitro-explosives. It can be performed fast, in a single working step without risks of contamination. The obtained solution can be analysed directly by gas-chromatography or HPLC.

The procedure has to be adopted to the matrix supporting the explosives traces. Dust or soil with a high carbon content have to be extracted at higher pressures for a longer time than swabs or glass splinters.

SFE is not selective to enrich explosives traces in the polarity range of the reversed phase HPLC analysis. Similar to other preparation methods selective detection such as GC-TEA is necessary. Further investigations have to be done to see whether selectivity may be controlled by the addition of modifiers or a stepwise extraction program.

In the future SFE will replace the classical liquid extraction methods for the sample preparation for analytical purposes in most cases.

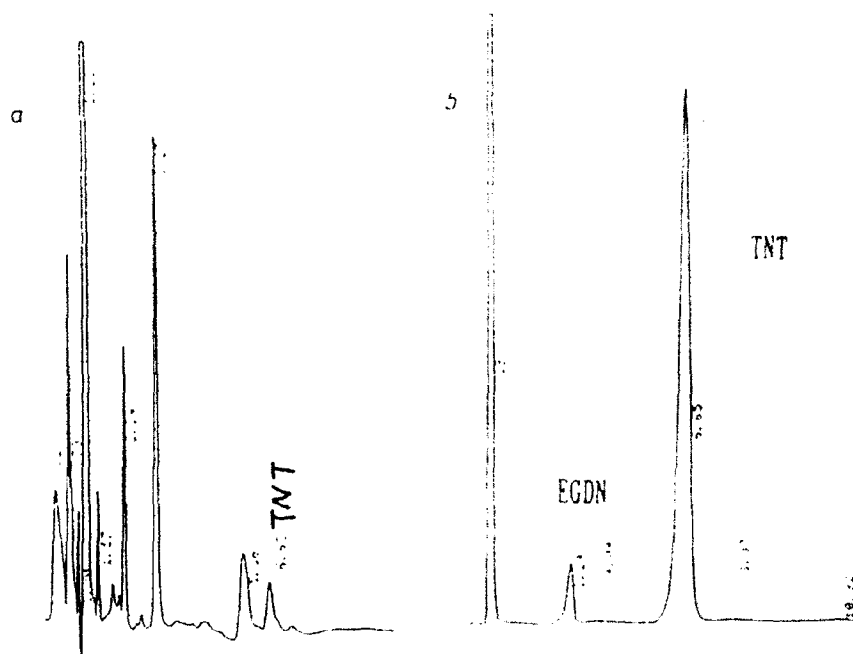


Figure 6: Analysis of explosive residues of a Donarit 1 charge
b) HPLC analysis of pure Donarit 1
a) SFE-HPLC of the residues obtained at 1m distance

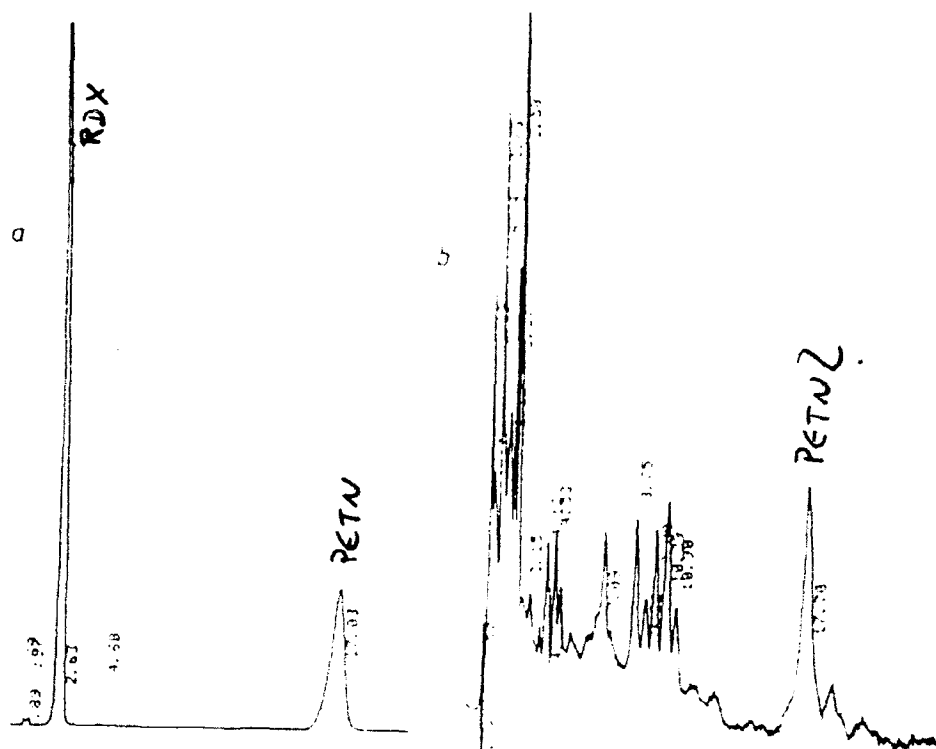


Figure 7: Analysis of a Semtex charge
 a) HPLC analysis of pure Semtex
 b) SFE-HPLC of the residues obtained at 1m distance

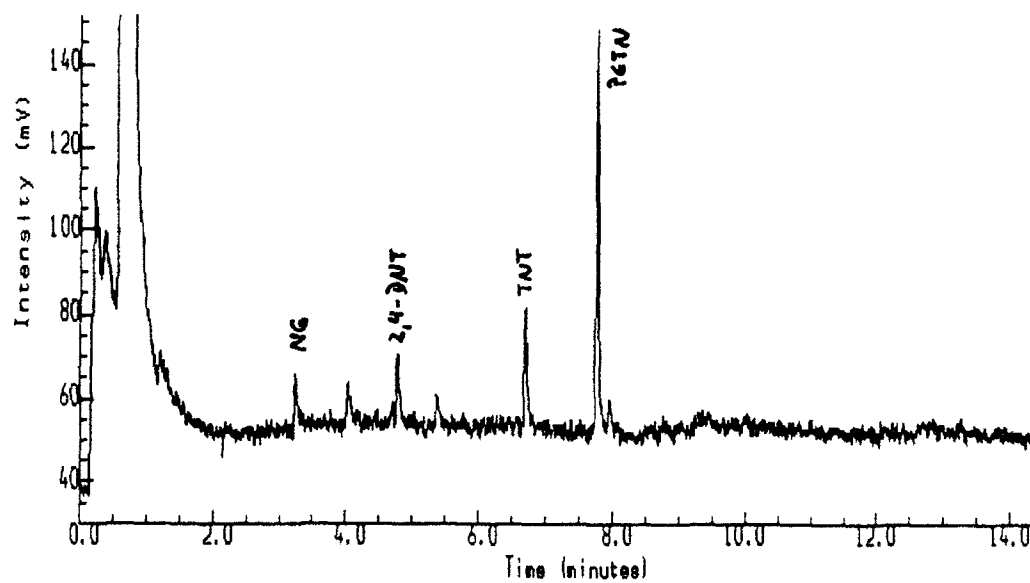


Figure 8: GC-TEA analysis of sample 7b)

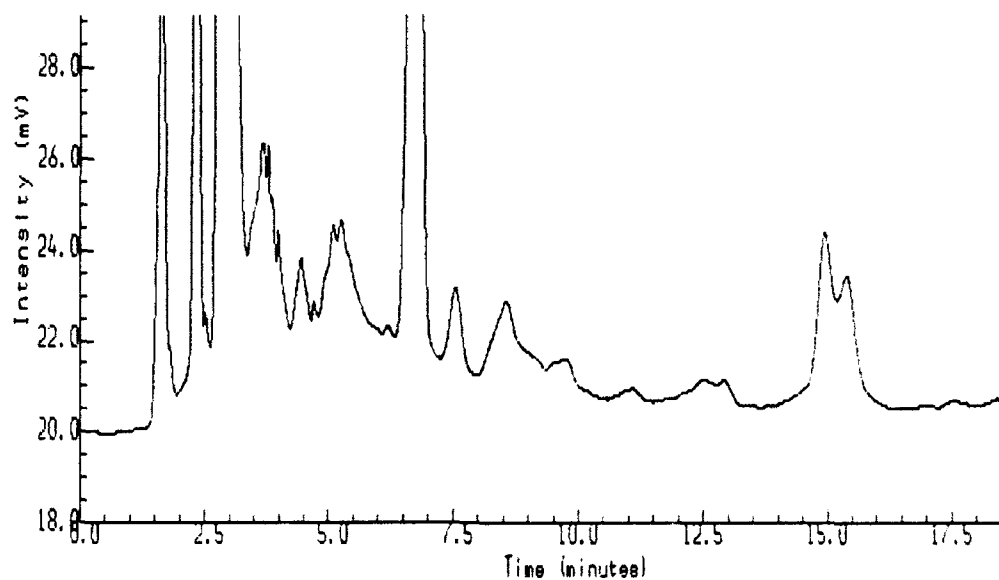


Figure 9a): HPLC analysis of vacuum cleaner dust

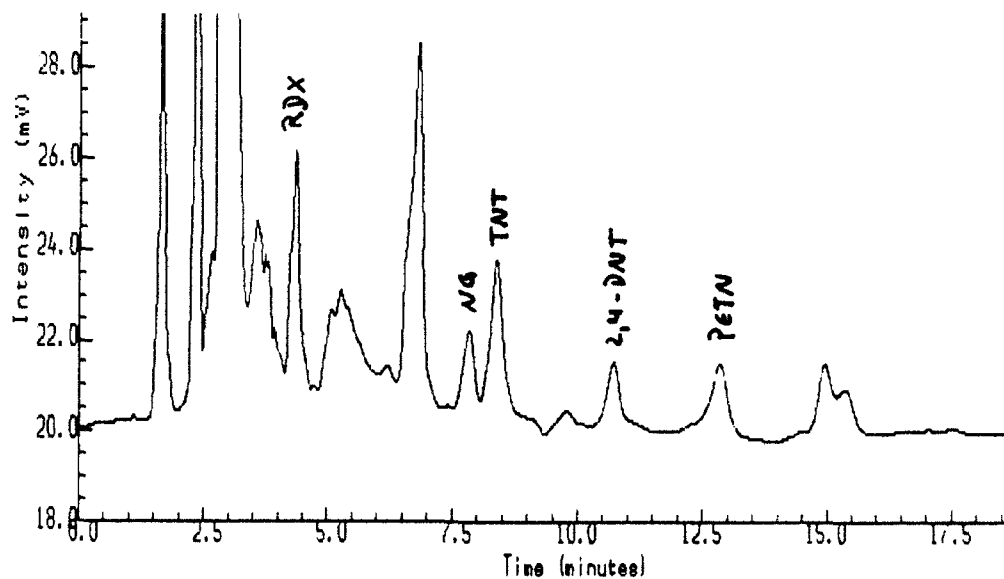


Figure 9b): HPLC analysis of vacuum cleaner dust spiked with explosives

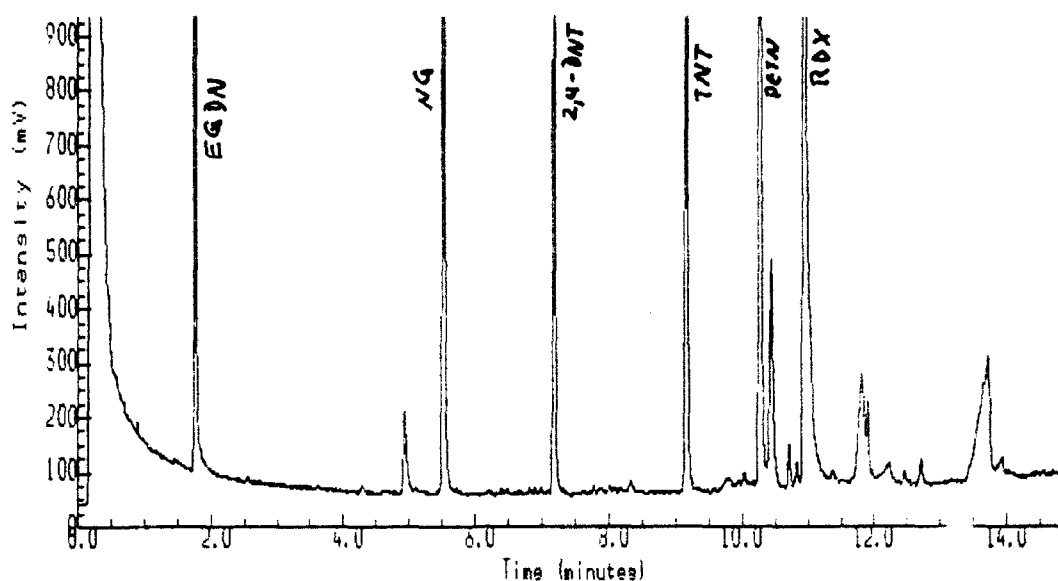


Figure 9c): GC-TEA analysis of vacuum cleaner dust spiked with explosives

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THE SEMTEX-H STORY

A W Feraday, OBE
Head of Forensic Investigations
Forensic Explosives Laboratory
DRA Fort Halstead
Sevenoaks, KENT TN14 7BP, England

ABSTRACT: This presentation is intended to give you an idea of the extent of criminal activities involving the use of SEMTEX explosive solely on mainland Britain (not NI) upto the end of 1989. The presentation might more appropriately be described as 'A CATALOGUE OF SEMTEX EVENTS', for that is what it is. Clearly the first question to answer is "When did we first encounter SEMTEX explosive in the Forensic Explosives Laboratory?"

To answer that I must ask you to think back over 19 years ago to try to recall what you were doing at 2.25pm on 11 March 1972. At that moment two small explosions were heard at the residence of the Jordanian Ambassador at 7 Palace Green Road, Kensington, London. Two watch operated time bombs had been placed, one at the front of the main entrance, the other on the windowsill of a large bay window. In both devices only the detonators exploded whilst the main charges, each of approximately 6lb ($2\frac{3}{4}$ kg) of explosive, had fortunately failed to explode.

When the fragments of the two partially exploded time-bombs were pieced together they showed two previously unencountered features. Firstly, the pieces of a moulded green plastics box and lid in the form of a time and power unit (TPU) which, with the recovered fragments of batteries, watch mechanism and detonator, had clearly been purpose built.

Subsequently we received some details and a sample of a similar TPU which had been seen in the Middle East.

The second novel feature about the two Jordanian Ambassador's Residence devices was that the explosive in both instances was an orange coloured plastic explosive with little odour, of a type we had not previously encountered. It was shown to have a very high explosive performance not unlike that of PE4 (C4) and to be based essentially on a mixture of RDX and PETN. Our dilemma of what to call this previously unencountered explosive was solved for us by the Metropolitan Police Explosives Officer's report on the incident which stated that when he first saw the explosive of the two devices, each had two elongated slabs of the orange explosive lying alongside each other, and that he thought at first that they were a pair of 'KIPPER' fillets. Henceforth for nearly a year the explosive was referred to by us as 'KIPPER EXPLOSIVE' until we traced its

manufacture to the SEMTIN GLASSWORKS of PARDUBICE, CZECHOSLOVAKIA and thus identified it as SEMTEX-H plastic explosive.

This isolated attack against the Jordanian Ambassador's residence was followed in late 1972 by a campaign of letterbombs directed against Jewish institutions in this country. Between September and November 1972, 21 letter bombs were airmailed in from Amsterdam, Singapore and India to leave one person dead and another seriously injured. These devices were claimed by the Palestinian "Black September" organisation.

The first of these letterbombs, which contained approximately 1.6oz (45g) of SEMTEX explosive, was received by 40 year old Dr Anis Shachori at the Israeli Embassy in Kensington where he worked as an Agricultural attaché.

The device partially exploded as he opened it whilst seated at his desk. He probably would have survived but for a splinter of wood from the table which unfortunately pierced his heart. Hence he became our first known victim of SEMTEX. The recovered fragments from this device included a spring loaded actuator mechanism and approximately 0.6oz (17g) of unconsumed SEMTEX explosive. There were seven other letterbombs sent that day, all of a similar pattern - enclosed in a greetings card with the actuation by means of a homemade percussion spring loaded striker mechanism - the release lever being held in place by a short length of copper wire for loading purposes. This wire was intended to be removed through the corner flap of the envelope after it was sealed down but in several cases this safety wire was still in situ when received by the intended victims. The investigating forensic scientist attributed this 'disarming' oversight to the perpetrators possible lack of "moral fibre". With hindsight this choice of words proved rather unfortunate since in his further correspondence with other foreign forensic scientists who were looking at similar devices received in their own country, it was asserted by one of them that "they could find no such fibres during their examination of the devices". This series of letterbombs was also intriguing in that, in order to manufacture them as thinly as possible, the open ended (plain) detonators used in many of them had been flattened by crushing them in a vice. The crushing of the nearly 3 grams of mercury fulminate and RDX present in these Russian detonators is a procedure which not unsurprisingly has ceased. In other instances the detonator was disassembled and its contents pressed into a recess in the SEMTEX explosive.

It was just over a year later in early 1974 before we again encountered "Kipper" explosive. On 24 January 1974 at 11 am a man stepped through the doorway of the Bank Haboalim in Lawrence Lane, London and hurled a bomb over the counter. It exploded within seconds, projecting many high velocity fragments of steel. It was very fortunate that no-one was seriously injured, with only structural damage to the building being caused, especially since the forensic examination that followed showed clearly that the device had consisted of a TNT-filled Russian F1 fragmentation grenade with about 9oz (250g) of SEMTEX explosive - as it was now being called - wrapped around it. Despite the violence of the detonation of the TNT and the major disruption of the grenade body, the SEMTEX had once again failed to detonate completely and was instead scattered in small pieces all around the premises.

Some four years passed before SEMTEX was again encountered on the mainland of Britain in an isolated letterbomb sent to the Iraqi Embassy in London. This letterbomb was essentially similar to that which killed Dr Shachori six years earlier.

On 1 June 1980 a SEMTEX based explosive device exploded at the offices of the Kuwait Oil Company in London. Forensic recovery from the debris revealed that a mechanical kitchen timer had been used in the actuation mechanism of this device. We were to encounter this particular type of mechanism seven times again over the next four years.

Six months later in December 1980 two similar explosive devices were defused at the London offices of the French Tourist Board. Each device consisted of a tape enwrapped SEMTEX charge of approx 5lb (2.5kg) weight intended to be actuated by a rather crude homemade transistorised electronic timer.

One year later on 13 December 1981 the three occupants of this white Datsun motorcar parked in Connaught Square, London were putting the finishing touches to a pipe bomb which was packed with 3oz (85g) of SEMTEX explosive taped up with over 300 steel balls in the form of an improvised Claymore device. One of the backseat passengers was gripping the pipe between his knees whilst the other backseat passenger lent over it. The device detonated prematurely, killing them both instantly. The majority of the steel balls were shot through the roof producing 283 penetrations through it. It appears that this device was intended to disrupt an anti-Khomeni meeting due to take place in Hyde Park that afternoon. The driver of this vehicle, who survived the incident, had the most appropriate name for such a disastrous bombing mission. His surname was FOOLADI. He received ten years imprisonment, and was subsequently released just before Christmas 1990.

Three years later, 10 March 1984, three devices were diffused in the Kensington area of London. Each device was essentially similar consisting of approx 3lb (1.4kg) of SEMTEX explosive with an electric detonator actuated from a modified kitchen timer. This timer being a Smither Timecal brand, similar to that employed four years earlier at the Kuwait Oil Company Offices.

Three days later on 13 March 1984 a device was discovered at the Omar Khazzam Restaurant in Kensington, London (presumably planted by somebody who did not like the decour!). The device consisted of a metal food tray packed with approximately 2lb (1kg) of SEMTEX and actuated once again by a modified kitchen timer.

In October 1984 there was a find of explosive materials in West London. Amongst this material were Russian F1 grenades and slabs of SEMTEX explosive. This recovery could be shown to be linked to the grenade and SEMTEX attack which took place against the Bank of Haboalim in January 1974 - over ten years earlier.

On 17 April 1986 a Jordanian named Nizar Hindawi packed a bomb into his pregnant girlfriend's suitcase before she went to Heathrow to travel by an El- Al flight to Israel. The device consisted of a 3lb (1.4kg) charge of SEMTEX explosive secreted into the false base of the suitcase. A functioning pocket calculator was used to conceal an improvised five hour delay electronic timer and a detonator inserted into a 2oz priming charge of SEMTEX. Explosive trials carried out at the time showed conclusively that had the primed calculator been in the bottom layer of the suitcase at the moment of detonation it would have sympathetically detonated the main charge secreted below it. Hindawi had deliberately placed a new battery in the calculator and packed it in the bottom of the suitcase whilst travelling with his girlfriend in a taxi to the airport. Hindawi's bomb would have undoubtedly exploded while the aircraft was in flight with devastating consequences but for the vigilance of the El-Al security staff at Heathrow. Hindawi's

miscalculation cost him 45 years.

It was not long after the first report from Ulster of the use of SEMTEX explosive by the Provisionals that there came the first clear indications that the PIRA were planning to use SEMTEX in their terror campaigns on the mainland rather than the commercial gelignites they had previously employed.

In February 1987 came the unearthing of a major cache of explosives, bomb making equipment and weapons from sealed dustbins buried in Macclesfield Forest and the nearby Delamere Forest. This find included time and power units, radio control equipment, detonators and 190lb (86kg) of SEMTEX explosive in its original sealed factory wrappers.

By now the name of the manufacturer in Czechoslovakia had changed from the Semtin Glass Works, to the Eastern Bohemian Chemical Works and then finally to Synthesia.

Despite, or perhaps because of, the discovery of this large haul by the Security forces, two months later in April 1987 a series of book-bombs containing SEMTEX was sent to six senior civil servants on the mainland.

They were fortunately ineffective not in small part because of the suspicious legends on their envelopes. But they were similar in design to ones that had appeared in Ulster in 1986, although those had contained gelignite explosive. Again an indication of the switch by the Provisionals to SEMTEX.

This so-called "Observers Book" series contained between 1 and 3oz (30g and 90g) of SEMTEX explosive, a detonator, two batteries and a modified watch-arming switch. The device was intended to function when a strip of insulating paper was removed from between two opposing strips of aluminium foil.

In late July 1987 the PLO were thought to have been responsible for the shooting of an outspoken political cartoonist outside his office in Chelsea. The subsequent search for the killer led to Hull where on 13 August 1987 a cache of bomb making equipment and 66lb (30kg) of SEMTEX explosive was recovered. This was a rather old worn-looking explosive. But what was of particular interest was the fact that it was wrapped in newspaper dated 17 March 1972 (ie 15 years earlier). You may (or may not!) recall that date, that is six days after the attack on the Jordanian Ambassador's residence - the very first incident of which I spoke involving SEMTEX on the mainland. Also recovered from Hull were green and black plastics moulded TPU boxes bearing MUNDO brand watches matching those of that previous incident.

On 2 August 1988 the first SEMTEX explosion attributed to PIRA on the mainland of Britain occurred when a bomb exploded at the Inglis Barracks, the Army Postal Sorting Unit in Mill Hill, N London. One soldier was killed and extensive damage to the building occurred.

An indication of further escalation in the use of SEMTEX by the PIRA occurred four months later on 21 December 1988 when, following an incident involving a car parked outside Staplehurst Court, Battersea, London, a search of one of the flats revealed 107lb (48kg) of SEMTEX explosive, and other terrorist paraphernalia. Some of the SEMTEX was already enwrapped by adhesive tape into discrete charges and appears to have been

intended for use with the TPUs present there. Also present were undercar devices complete with their attachment magnet and SEMTEX explosive.

Also on that same day 21 December 1988 there occurred the single most devastating terrorist event involving the proven use of SEMTEX explosive when PANAM Flight 103 en route from London to New York was blown out of the sky, falling predominantly on the Scottish village of Lockerbie. 270 people died that evening including 11 residents of Lockerbie. I can say little about the Lockerbie incident at the moment for legal reasons, save that the explosive traces recovered from some of the shattered debris are consistent with the detonation of a SEMTEX explosive charge, and that this charge was concealed inside a radio set situated in a suitcase present in a baggage container in the hold of the aircraft at the moment of detonation. The tragedy of Lockerbie will live forever in the memories of all those involved with this horrific incident.

As if Staplehurst Court and Lockerbie were not enough for the Forensic Explosives Laboratory to contend with, 1989 opened with a bang, or more correctly, with three bangs, when three explosions occurred at the Army's Ternhill Barracks in Shropshire. Severe damage occurred to some of the buildings but fortunately the occupants had been roused from their beds following a confrontation with two terrorists by a vigilant camp guard. Hence, luckily there were no fatalities.

On 27 February 1989 there was a recovery of 10kg of SEMTEX explosive from a Thames Waterboard reservoir in N London. It appears most likely that this material was related to the PIRA recovery from the flat at Staplehurst Court two months earlier.

On 8 March 1989 some terrorist materials were discovered partially buried in the Broxa Forest, N Yorkshire. This find included not only 7.5kg of SEMTEX explosive but also two improvised fragmentation grenades each containing approximately 5oz (140g) of SEMTEX explosive. This was further confirmation of the diversity in the use to which the PIRA intended SEMTEX.

On 22 September 1989 there occurred a violent explosion at the Barracks of the Royal Marines at Deal, Kent which killed ten bandsmen instantly and an eleventh who died of his wounds one month later. This incident, like most of those to which I refer in this latter part of this presentation, is under active investigation and details concerning it are sub-judice, but I can reveal that the recovered traces of the explosive used at Deal are consistent with the detonation of a SEMTEX charge.

On 10 October 1989 a man walking his dog in Hampstead Heath discovered two holdall bags scarcely hidden under some bushes. The bags contained a total of 100lb (45kg) of SEMTEX explosive some of which was already prepared into two tape wrapped bundles each of 25lb (10kg), possibly intended to be used as radio controlled bombs activated from the two main control units present in the find. The remaining 50lb (25kg) of SEMTEX was in the form of individual 5lb (2.5kg) blocks and these may have been intended for make-up into under-car devices together with those powerful magnets.

Between 3-8 November 1989 two caches of PIRA bomb making equipment and materials were uncovered along a coastal path in Pembrokeshire, Wales. These two adjacent caches contained a total of 80lb (36kg) of SEMTEX explosive, much of it in its original factory wrappings, and also many electronic timing units and powerful magnets. Once again it appears that undercar devices may have been the intended use for these materials.

Five days after the second discovery in Wales, ie on 13 November 1989, a PIRA undercar device was defused in Kelso Place, Chelsea, London. The device appears to have been intended for a high ranking Army Officer although it was in fact placed on the wrong car. The device contained over 2lb (900g) of SEMTEX and a watch delay arming system with a mercury tilt operating switch. Possible correlations of this device with previous incidents cannot be discussed at this stage.

Five days later, on 18 November 1989, an undercar device exploded against this Volkswagen motorcar, driven by an Army Sergeant as he started to back it out that morning. The device, which appears to have been similar to that at Kelso Place five days earlier, caused severe injuries to the Sergeant including the loss of both his legs. Explosive traces were recovered consistent with the detonation of a SEMTEX charge.

On 23 December 1989 two Irishmen were arrested when they returned to the Pembrokeshire find, the discovery of which had been kept secret for seven weeks. A search of a Luton address occupied by these two men revealed 7.5kg of SEMTEX together with electronic timers and radio control equipment.

Whilst that concludes the catalogue of the use of SEMTEX in terrorist devices on the mainland of Britain upto end of 1989, I should like to give you a brief overview. In general summary:

1. We have seen a considerable increase in the use of SEMTEX on the mainland during the past 20 years.
2. There has been a change in the pattern of use of SEMTEX, commencing with small emplaced watch operated devices through to the current vogue for undercar devices, improvised grenades and radio control devices (and latterly projected mortars).
3. Whilst not wishing to push statistics to you, I have briefly just described all 58 SEMTEX incidents which we have experienced in the Forensic Explosives Laboratory over the past 20 years. These have caused the deaths of 284 people. In that same period we have examined 3288 explosive incidents involving explosives other than SEMTEX. These have resulted in the deaths of 107 people. Clearly the deaths figures for SEMTEX are grossly distorted by the horrific Lockerbie incident without which we would have recorded only 14 deaths for SEMTEX of which Deal barracks accounts for another 11. Although one death is too many I should just like to convey that out there on the streets over the past 20 years there has been more going on without the use of SEMTEX than there has been with it. However, clearly SEMTEX, like any other explosive, has great potential to kill when placed in the wrong hands.

But the bottom line is, if we managed to solve all the problems of SEMTEX, another equally lethal explosive would be found to fill its place.

THE IDENTIFICATION OF ORGANIC PEROXIDES

J. CHLADEK

Laboratory of Federal Criminal Police.

P.O.Box 16

182 00 Praha 82

Czechoslovakia

ABSTRACT. There are two significant explosives belonging to the group of organic peroxides, namely triacetonetriperoxide (TATP) and hexamethylenetriperoxidediamine (HMTD). Previous studies showed that TATP and HMTD are not stable enough to find an application in commercial or military sphere.

Organic peroxides are interesting for forensic chemists, because of the obvious possibility of utilization of TATP or HMTD by terrorists.

These peroxides contain neither metallic elements, nor nitro group. Therefore their presence cannot be detected by standard security procedures (transmission RTG, vapor detector etc.).

Preliminary examination is possible by odor, spot tests etc. Identification of these explosives is realized by thin layer chromatography (TLC).

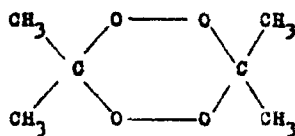
1. Introduction

An explosive properties of the organic peroxides were in details examined in the past due to the fact that some of them (namely acetoneperoxide - ACP and hexamethylenetriperoxidediamine - HMTD) belong to the explosives. An attention was focused among others to their possible application in military and civil blasting technology. A possibility of utilization of HMTD in production of the detonators was examined as well. However, due to their low physical or chemical stability and high sensibility to the mechanical shock, peroxides did not find a practical application.

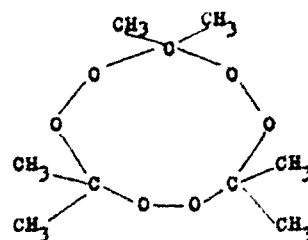
Nevertheless, it is a group of substances which draw an attention of forensic scientists as these substances are used in criminal activity and by terrorists.

Their utilization is preferred for quite simple production manageable under quite provisional condition of "home laboratories" and ordinary available raw material necessary for the production.

The basic raw materials necessary for the production of ACP are acetone and hydrogen peroxide. During the reaction a dimer- acetoneperoxide (acetoneperoxide, ACP) I, trimer-acetoneperoxide (triacetonetriperoxide, TATP) II and a small quantity of the by-products.



I dimer



II trimer

The most of HMTD manufacturers (approx. 95 %) utilizes the reaction of urotropine (hexamethylenetetraamine), which could be bought in CSFR as the fuel for tourist cookers, with hydrogen peroxide catalyzed by citric acid.

Although these explosives are easily available and powerful (especially HMTD) there have not yet been recorded any case of utilization of these peroxides for the terrorist purposes. The peroxides are utilized mainly for home production of petards (blasting balls) and there were some cases of home production of detonators and plastic explosives on the bases of HMTD. A lot of injuries is caused already during production itself and further processing.

In 1991 there was recorded a case of spontaneous ignition of HMTD during drying of the raw material produced under provisional conditions.

2. Analytic Procedures

2.1 PRELIMINARY TESTS

- Freshly manufactured ACP has a pleasant fruit-like smell. Old or technologically not pure HMTD often smells of formaldehyde.
- A characteristic property of ACP is a sublimation. No other explosive of white color has such a property.

A small quantity of this substance is spread on the glass slide of microscope and covered by another glass slide. After heating (sufficient is the radiation heat of spot lamp of microscope) the ACP "travels" to the cooler place within the glass slide.

- A preliminary identification of peroxides can be made by test in the flame. This test however requires some degree of experience.
- For the preliminary identification also a spot test can be used. The reaction is carried out on the white spot plate. It is necessary to make a blank test. To the small quantity of tested substance a several drops of acetone are added and 1 - 2 drops of saturated solution of anilinhydrochlorid in concentrated hydrochloric acid. ACP shows blue-green color. Adding 1 - 2 drops of 1% TSS (N,N - diethyl - p - phenyldiaminesulphate) water solution HMTD results cherry-red color, ACP pink.

2.2 IDENTIFICATION

A definite identification of ACT and HMTD is carried out by thin layer chromatography under the following conditions:

Plate: TLC plates silica gel 60, 5 x 10 cm (Merck, Art. 5719)
10 x 20 cm (Merck, Art. 5729)

Sample aliquot: 1 μ l

Solvent: acetone

Eluent: benzene

Elution distance: 80 mm

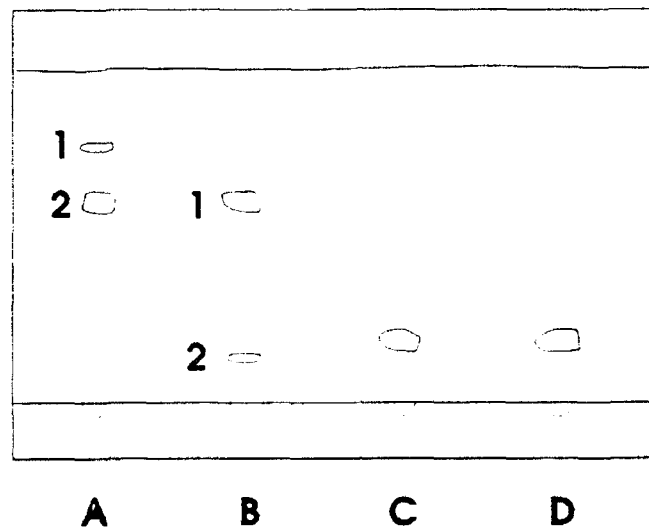


Fig. 1 Chromatogram of organic peroxides

A - ACP freshly prepared

B - ACP old (more than 2 weeks)

C - HMTD freshly prepared

D - HMTD old (more than 2 weeks)

2.2.1 Detection and detection limits. A detection is carried out spraying the substance by solution of detection agent and consequent heating up to 100 °C in duration of 5 minutes. The detection limits are influenced by the quality of tested peroxide. As a detection agent the following is used:

- A saturated solution of anilinhydrochlorid in concentrated hydrochloric acid. The detection limit is for ACP $2 \cdot 10^{-5}$ g, for HMTD 10^{-7} g.
- A freshly prepared 1% solution of TSS in distilled water. The detection limit is for ACP $4 \cdot 10^{-6}$ g, for HMTD $5 \cdot 10^{-8}$ g. During ageing the remarkable loss of sensitivity occurs already after several minutes.
- 1% solution of diphenylamine in nitrogen-free concentrated sulphuric acid. The detection limit for ACP is $7 \cdot 10^{-8}$ g and for HMTD $2 \cdot 10^{-7}$ g.
- 1 % solution of thymol in nitrogen-free concentrated sulphuric acid. The detection limit for ACP is $3 \cdot 10^{-8}$ g and for HMTD is $5 \cdot 10^{-8}$ g.

3. Discussion and Conclusion

During the tests it was found out, that the substance which provides the spot A_1 is during the ageing loosing (remarkable loss is evident already after one week) and the substance which provides the spot A_2 identical with the spot B_1 is completed by the substance B_2 . Based on the gained results there was a hypotheses expressed saying that the spot A_1 is provided by trimer (TATP), the eight-member circuit of which is unstable and therefore is transferred into the dimer (ACP) with more stable six-member circuit (trace A_2 and B_1) and decomposed products B_2 .

At present stage of rapid development of a detection technology and resulting advanced explosive detectors it is possible by suitable combination of the individual systems to detect with a high rate of probability actually all types of military and industrial explosives. However this is not true if concerns the organic peroxides.

Especially HMTD is predicted to become an feared explosive of professional terrorists. Its power, comparable with series of military and industrial explosives, easily procurable raw material, simple production and on the opposite side difficult detectability at security check-ups and limited stability of post blast residue. These are the properties by which the HMTD sells itself directly to the terrorists.

From this reasons it is necessary to continue studies of selected organic peroxides. This will increase the probability of their detection by security check-ups and the procedures of post blast residues securing, transporting a processing in laboratories (development of a new method with increased sensitivity) will be further improved.

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Slurry and Emulsion Explosives: New Tools for Terrorists, New Challenges for Detection and Identification.

Charles R. Midkiff Jr. and Allan N. Walters

*Forensic Science Laboratory, National Laboratory Center, BATF Rockville, Maryland and
U.S. Postal Service Laboratory, Washington, DC respectively.*

Abstract

With advantages in cost, safety and ease of use, water gel/slurry and emulsion explosives are rapidly replacing traditional explosives. As a result, cap sensitive versions of each are increasingly encountered in criminal activity and a strategy for their identification and characterization is needed. A water gel/slurry explosive is essentially an aqueous solution of an inorganic oxidizer gelled with a carbonaceous gelling agent. Dispersion of fuel or additional oxidizer in the gel produces a slurry, the "water gel explosive" of commerce. Added sensitizers enhance initiation to a detonator with particular compounds protected by patent and specific to a producer. When intact material is available for examination, sensitizer and other component identification characterizes the explosive type. Emulsion explosives, more efficient than gels, differ in that, emulsifying agents suspend droplets of aqueous oxidizer solution in an oil phase. Chemical sensitizers may be used in emulsion explosives but are less common than in slurry types. Most emulsions are sensitized by microspheres, tiny glass bubbles which both control density and provide "hot spot" initiation. Physical characteristics and composition of typical slurries and emulsions, combined with a systematic analytical approach, are used for the characterization and discrimination of intact gel/slurry and emulsion explosives.

Introduction

For reasons of safety, storage and economics, in the past two decades, commercial makers and users of explosives have moved away from traditional high explosives such as dynamite. As a result of decreased use of this once widely available explosive, the explosives used in criminal and terrorist incidents are changing. In the early 1970's, the principal explosive encountered in the ATF laboratories was commercial dynamite [1]. While dynamite is now far less frequent in criminal bombings in the United States, its commercial replacement, the slurry or emulsion explosive, is increasingly being encountered as criminals become familiar with these newer types of high explosives.

In North America, and to an increasing extent worldwide, for large scale commercial blasting, mining, construction etc., the major volume high explosives today represent a radical departure from traditional explosives' concepts. Whereas water represented a problem to users of dynamites and blasting agents such as ANFO, its successors have water as a significant component.

Gel or Slurry Explosives

A more recent explosive, resembling a gelatin dessert, is referred to as either a water gel or slurry. Rigorously, most are slurries because they contain one or more solid components suspended in a continuous semi-solid or gel phase. No clearcut distinction between gels and slurries appears to be made within the explosives industry and for convenience, the terms will be considered synonymous. These explosives consist essentially of a water solution of an inorganic oxidizer such as ammonium nitrate, or for better density control or sensitivity, mixtures of ammonium with sodium or calcium nitrate, gelled with a natural polysaccharide such as guar gum. Additional crystalline oxidizer and fuel is suspended in the gel matrix. Other ingredients may be added as fuels, sensitizers, stabilizers, etc. Common components of water gel/slurry type explosives are listed below.

Table 1

Ingredients for Slurry Explosives

Ingredient	Function		Ingredient	Function
NH ₄ NO ₃	Oxidizer		Guar gum	Gelling Agent
NaNO ₃	"		Starch	"
Ca(NO ₃) ₂	Oxid./Density		KCrO ₄	cross-linking
NaClO ₄	Oxid./Sens.		Sb comp'd	"
Microspheres	Density/Sens.		Bi "	"
Amine nitrate	Sensitizer		Boric Acid	"
Glycol nitrate	"		Borax	"
flake TNT	"		Aluminum	Fuel/Sensit.
Smokeless pwd	"			

Additional explosive and non-explosive components considered for use in slurry explosives are listed by Sudweeks [2] and Kaye [3].

A more modern, but related, water containing explosive, the emulsion, differs from the gels in that emulsions consist of two distinct phases, an oil phase and a water phase. These too, are increasingly becoming tools for criminal or terrorist activity and their characterization will be discussed subsequently.

Slurry/gel or emulsion explosives capable of direct initiation by a number 8 detonator or blasting cap are classified as cap sensitive and subject to rigorous handling and storage requirements. Slurry/emulsion explosives not initiated by a No. 8 cap, are classified as blasting agents and subject to less restrictive regulation. These require a primer for initiation but, once initiated, usually have detonation velocities in the high explosive range. Blasting

agents are infrequently encountered in our laboratory but can be characterized using the approach to be described.

Cap sensitive slurries were first used for commercial blasting in Canada about 1957 [4] but about two years earlier, water gel explosives sensitized with N,N-bis (trinitroethyl) urea and capable of initiation by a No. 8 detonator had been developed in Sweden [5]. Initially, North American slurry explosives were sensitized with high explosives such as TNT, low explosives such as smokeless powder or with flake aluminum [6]. A variety of other materials, both explosive and non-explosive, were proposed and/or used by explosive producers as slurry sensitizers during the 1960's but most were not completely satisfactory. Although attractive for a variety of applications, early gels had a number of limitations. Among these was the tendency of ingredients to segregate at elevated temperatures or for the oxidizer to salt out at low temperatures, rendering the explosive ineffective. Addition of surfactants and use of calcium nitrate as a co-oxidizer improved low temperature sensitivity. Cross-linking of the gelling agent with boron, antimony or bismuth compounds produced a gel of improved stability and largely solved both segregation and salting out problems [7]. A second major advance in water gel explosives was the introduction in the mid 1960's of sensitizers such as nitrate salts of hexamine, ethanolamine or monomethylamine, although at the levels used to achieve adequate sensitivity, they should be considered as significant components in the final product. Because each sensitizer is covered by patent, identification of the sensitizer compound, if any, is an effective method for identification of the producer of a gel explosive. **Table 2** contains a representative listing of sensitizers for slurry explosives, including some no longer used but which could be encountered in old products.

Table 2

Chemical Sensitizers for Slurry Type Explosives

Company	Brand Name	Sensitizer	Ref.
Dupont/ETI	Tovex	Mono Methylamine Nitrate	26
Hercules	Flogel	Smokeless powder (DNT optional)	31
Hercules/IRECO	IREGEL	Mono Ethanolamine Nitrate	27
Thermex/SEC	Detagel	Hexamine Nitrate	28
IRECO	IREGEL-435	Aluminum	3
C.I.L.	Powermex	Ethylene glycol mononitrate	19
Trojan/IMC	Trojel	Nitrostarch	3
ICI/Nobel	Supergex	Isopropyl nitrate	29

In addition to chemical sensitizers, slurry/emulsion type explosives are also sensitized by voids in the form of tiny bubbles. Air may be entrained at the time of mixing or bubbles produced by reaction of additives. Reproducible entrainment; however, is difficult and entrained gas is less effective as a sensitizer at low temperatures. In addition, problems arise when the explosive is subject to hydrostatic pressures, as for example, a column of cartridges loaded vertically in a borehole. Current practice relies on incorporation of hollow glass, resin or ceramic spheres known as microspheres or microballoons. These micron-size spheres serve two functions in explosives; they may be added to control density, critical for detonation wave propagation, or function as either a primary or secondary sensitizer. Glass spheres are transparent, resin spheres translucent and ceramic types are opaque. With few makers of microspheres and different types of glass used, producers are distinguishable. This information can be of value when a rigorous comparison is required, as for example, comparing a sample obtained from a suspect with a sample of known source. While microspheres have other applications, for example, as a filler in epoxy potting compounds, their wide use in slurry/emulsion explosives is a useful indicator that the material being examined is one of these.

Most major explosives producers consider the formulations of slurry or gel explosives proprietary so little compositional information is found in the literature to aid the analyst in characterization of these materials. Information on ingredients and expected concentration ranges is best obtained from the original patents. Kaye [3] has an extensive listing of slurry explosive related patents with patent title, number, and name of company to whom assigned but its coverage is only prior to 1980. One of the authors (CRM) is preparing a listing of patents dealing with slurry and emulsion explosives to expand the coverage to more recent products which, when completed, will be available on request. For illustration purposes, **Table 3** shows nominal compositions, obtained from published information, for several former and current commercial gel/slurry explosives.

Cap sensitive slurry type explosives are generally packaged in plastic bags or tubes and resemble commercial sausage packaging when intact. Cartridges range in diameter from 1 to 4 inches and 8 to 16 inches in length. Polyethylene, polyvinyl chloride and polyester films are used for packaging and the tubes may be clamped at each end with a small metal band. For former DuPont products (now made by ETI), a blue colored sleeve indicates a permissible explosive, i.e. one approved for use in underground coal mines.

Emulsion Explosives

One of the newer commercial explosive developments, competing with both commercial dynamite and the water gel slurries is the cap sensitive emulsion. In these water-in-oil emulsions, a droplet of a supersaturated solution of ammonium nitrate is surrounded by a hydrocarbon serving as the fuel. A typical emulsion consists of water, one or more inorganic nitrate oxidizers, oil (with or without dissolved wax) and emulsifying agents of the water-in-oil type. Emulsions may contain chemical sensitizers such as metal perchlorates to improve initiation at low temperatures but often rely on microspheres for sensitization as well as density control. The size of the spheres exerts a significant effect on the sensitivity and detonation velocity of the explosive [8-9]. In a study of emulsions prepared with sieved

Table 3

Nominal Composition of Sensitized Slurries

Product	Producer	NH ₄ NO ₃	NaNO ₃	Sensitizer	H ₂ O/gum/Al	Misc
Hydromex	C.I.L.	38%	25%	25% TNT	12%	
DBA-1	IRECO	50	15	25 TNT	10	
Tovex 300	Dupont/ETI	30.8	14	36.7 MMAN	19.5	
Tovex 800	"	43	8.5	20 "	29.5	
SSS	"	18	6.7	35.3 "	22.1	10*
TR-2	"	23.5	13.2	30 "	32.3	
CS Booster	Hercules	38.2	-	33.5 EGMN	18.6/1.0/-	#

* Calcium nitrate

Ethylene glycol/crosslinking agent/microspheres (4.2/0.5/4.0)

spheres, velocities obtained with 64 μ m spheres were considerably higher than with those of 82, 108, 111 and 153 μ m and velocity fall off with increasing density was much less severe [10]. Several years ago, it was indicated that "All emulsions manufactured at Atlas now use bubbles or microspheres for sensitizers" [11], however, our laboratory has also identified perchlorates in Atlas Powermax formulations so the possibility of additional sensitizers in an emulsion should not be overlooked. Additional samples will be examined to determine if secondary sensitizers are a standard ingredient for a particular product or are added, as needed, for improved low temperature sensitivity to ensure reliable initiation in cold climates. The consistency of most emulsions resembles that of cream cheese and they may or may not be aluminized. In general, the aluminum in emulsions is discrete granules, as compared to the fine paint-grade or atomized material used to increase the energy of slurries. Representative ingredients of emulsion explosives are shown in Table 4.

Until recent years, Atlas enforced its basic patents [12-13] and was the only U.S. domestic producer of emulsions. Because emulsions release 93% of their calculated thermochemical energy versus 50-70% for gels, they are extremely attractive on a cost/performance basis and, in addition, exhibit excellent storage stability. As a result, since expiration of the Atlas patent, emulsion explosives have become available from most major manufacturers and numerous patents on emulsion explosives worldwide have been located in a survey of the *Chemical Abstracts* database. Emulsions may be packaged in plain Kraft, waxed or plastic coated paper cartridges closely resembling commercial dynamite. Package sizes range from 1 to 3 1/2 inches in diameter and 8-16 inches long. An interesting difference between

Table 4

Ingredients for Emulsion Explosives

Ingredient	Function		Ingredient	Function
NH ₄ NO ₃	Oxidizer		Paraffin Oil	Fuel
NaNO ₃	"		Microchrystl. Wax	"
Ca (NO ₃) ₂	Oxid./Density		Paraffin Wax	"
NaClO ₄	Oxid./Sens.		Aluminum, granular	"
Microspheres	Density/Sens		Sorbitol esters	Emulsif
Amine nitrate	Sensitizer		Sorbitan esters	
Diesel fuel	Fuel		Oleates, various	"
Tall Oil	"		Ethanolamides	"

permissible emulsions and dynamites is that the dynamite usually contains several percent of sodium chloride to suppress flash whereas sodium chloride may not be needed in the permissible emulsion. One example of a permissible emulsion is Atlas 7D.

A variety of two component emulsification systems have been described in patents for emulsion explosives. Despite the usage level, usually less than 2%, of these in the finished product, identification of the emulsifiers is an area for further study. Particular combinations, as for example, Sorbitan sesquioleate and oleic diethanolamide, may be consistently used by a manufacturer and serve as a guide to producer identification.

Combinations of oxidizers are frequent in emulsions and to further reduce dust initiation in mines, emulsions have been made with complete replacement of the ammonium nitrate component by sodium or calcium nitrate [14]. Although compositionally quite similar, there are a range of emulsion formulations, depending upon desired performance. Nominal compositions of several emulsions are shown in Table 5. For these, except as indicated, the formulation is for the basic emulsion and microspheres are added to obtain the desired density.

Laboratory Examination

When a sample of a suspected water gel slurry or emulsion is received in the laboratory, visual examination provides an indication of its type. Typically, water gels have a consistency resembling that of set gelatin or gel-type toothpaste and range from nearly clear, often with suspended white particles, to an off white or cream color. Aluminized slurries are silver grey. Emulsions are frequently off white in color and may contain visible aluminum

Table 5

Nominal Composition of Emulsion Explosives

NH ₄ NO ₃	NaNO ₃	H ₂ O	Emulsifier	Oil/Wax	Oxidiz.	Ref
78.7%	-	16.0	1.5	3.8	-	9
66.91	-	12	1.5	5.0	14.59 ^a	10
78.9	-	15.8	1.5 ^b	3.8 ^c	-	8
57.8	17.4	15	1.5/0.6	4.3	-	23
64.22	2.85	11.4	0.95	2.85/0.95	9.88 ^c	13
67.6	3.0	14.0	1.0	1.0/3.0	10.4 ^d	13

a Calcium nitrate

b Estimated (total oil and emulsifier 5.3%)

c Sodium perchlorate; plus Aluminum 5.00% & glass bubbles 2.0%

d Sodium perchlorate; two types of wax - 1.5% of each

granules. For initial examination, a small portion of the original sample is placed directly on a microscope slide and examined at 30-40X. Observation of small spheres, often of different sizes and resembling bubbles, suggests a slurry or emulsion explosive. In addition, shiny particles of aluminum or grains of inorganic nitrates may also be visible. Several grams of the slurry or emulsion sample in a vial is shaken with 2-3 mL of hexane or pentane. The water gel or slurry will be essentially unchanged but the emulsion will disintegrate immediately. If the sample is tentatively identified as a gel or slurry, a few grams of the sample are diluted with water and placed in an ultrasonic bath for about 15 minutes to disrupt the gel structure or, alternatively, a small homogenizer can be used. Ten percent nitric acid has been suggested for destruction of the gel structure [15] but in our laboratory, for qualitative purposes, has not been found necessary. The sample is filtered or, more satisfactorily, centrifuged and the aqueous filtrate removed. When centrifugation is used, intact microspheres float on the surface and are collected using a pipette. They are deposited on a glass slide for optical microscopy or on a stub for examination by Scanning Electron Microscopy/ Energy Dispersive X-Ray (SEM/EDX) or alternatively, by X-ray Fluorescence. In the U.S., there are two major manufacturers of hollow glass microspheres, differing in composition, allowing the producers to be distinguished. This information is useful in sample comparisons. **Table 6** shows elemental analysis results for several types of microspheres.

The aqueous layer is removed and tested for nitrate with the modified Griess test and for ammonium with Nessler reagent. Testing for chloride with silver nitrate is useful because NaCl may be used in a permissible formulation or to increase density. A flame test will identify sodium and, with a cobalt glass, potassium, if present. If a small spectroscope is available, characteristic calcium lines may be observed with formulations containing calcium nitrate. Ion chromatography (IC) of the aqueous extract readily detects

Table 6

Elemental Analysis of Microspheres

<i>Producer</i>	<i>Type</i>	<i>Brand Name</i>	<i>Elements by SEM/EDX</i>
3M	glass	Scotchlite B23/500	Ca, Si, B*
PQ	glass	Q-Cell	Na, Si
PQ	ceramic	Extendspheres SG	Al, Ca, Fe, K, S, Si, Ti
Unknown	phenolic	unknown	Al, Cl, I, Na, S, Si
Unknown	glass	from Hercules	Al, Ca, Cl, K, S, Si

*with light element detector

ammonium, sodium, calcium, nitrate, and monomethylamine [15]. Although not essential with bulk samples, IC is convenient and routinely used in our laboratory. Ammonium and sodium nitrate can be identified when a portion of the aqueous extract is evaporated to dryness and examined by X-ray diffraction. Examination of a portion of the filtrate by AA or ICP spectrometry may detect antimony or bismuth, compounds of which are used in cross-linking the gel but has not been evaluated in our laboratory. Similarly, boron compounds may be detectable by addition of methanol to the filtrate and passage of the vapor, containing the volatile methyl borate into a flame.

If they have not previously been removed, the residue from the water extraction can be examined microscopically for microspheres. When suspected aluminum particles are observed, they are tested on a microscope slide with one drop of 10% NaOH. A separate portion is tested with 6N HCl. Aluminum reacts readily with NaOH to release bubbles and HCl reacts after an induction period. For definitive comparison of two samples, the morphology of the aluminum particles can be examined on the electron microscope.

Amine salts used as sensitizers are detected in the water extract. Parker [16] has described a modified spot test for primary and secondary amines to detect monomethylamine nitrate (MMAN) with a limit of detection of about 20ug and reports that ammonium nitrate does not interfere. Parker also describes a TLC method for MMAN using cellulose plates and a chloroform/methanol/water eluent. Visualization is based on detection of the nitrate salt with oversprays of diphenylamine (DPA), UV light and H₂SO₄ with an LOD of 0.5ug. Three different TLC systems for MMAN and monoethanolamine nitrate (MEAN) on cellulose or silica gel separate the amine nitrates from sodium and ammonium nitrate [17]. Eluent systems were chloroform/methanol/water, chloroform/methanol and chloroform/ethanol/water/HCl. Visualization was by overspray with ninhydrin and heating to develop the color or by the UV fluorescence of the derivative formed with the amine and fluorecamine. A less expensive alternative to fluorecamine, which we plan to evaluate, is o-phthalaldehyde.

More convenient than testing the filtrate is direct extraction of a portion of the intact slurry with methanol, which, while dissolving some ammonium nitrate, in TLC, is easier to work with than an aqueous extract. A cellulose plate (Avicel F, Analtech Inc. or equivalent) is used with a solvent of $\text{CHCl}_3/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (50:45:7) and initially developed with an overspray of 0.15% ninhydrin in freon. Heating of the plate visualizes the amine salt as rose-red but the spot frequently exhibits streaking. The plate is then sprayed with Diphenylamine in ethanol and exposed to long wave UV. Both the amine spot and that from the ammonium nitrate appear as lavender spots with NH_4NO_3 having a R_f in this system of about 0.19.

Although we have examined a number of TLC systems, varying plate type and mobile phase, further work is needed to improve spot structure, obtain a R_f higher than 0.34 for MMAN, and to evaluate the TLC behavior of other amine nitrate sensitizers. Spray reagents giving different colors with amino acids of different structure have been reported and merit evaluation.

Another approach to the detection of MMAN is extraction of the salt, formation of a TNBS [18] or dansyl derivative and identification by high-performance liquid chromatography (HPLC) using UV detection at 254 nm. With this approach, MMAN was detected in a water extract of a fragment of plastic film wrapper from Tovex [19]. We have similarly identified MMAN in an empty Tovex wrapper by swabbing with methanol and examining the extract by TLC. Prime and Krebs [19] detected the sensitizer, ethylene glycol mononitrate, in debris from explosion of the water gel slurry, Powermex. A purge-and-trap collection procedure on charcoal, and direct injection on the HPLC was used. Sensitive detection of MMAN and MEAN using HPLC with photolysis and electrochemical detection has also been reported [20]. In this work, a water extract containing the sensitizer is derivatized with 2,4-dinitrofluorobenzene and the effluent from the HPLC examined with and without photolysis prior to electrochemical detection. The amine derivative is detectable only in the "lamp-on" position of the photolysis unit. In IC analysis, addition of methanol to the mobile phase is reported to improve separation for MMA and monoethanolamine [21] but poses problems with swelling of some types of ion-exchange resins. A method for quantitative IC analysis of the amines and nitrates in water gel explosives is used by an explosives producer for routine quality control [15]. IC also permitted the determination of the relative concentrations of Na^+ , NH_4^+ , K^+ and MMA to distinguish two apparently similar water gels [22].

For emulsions, the hexane or pentane extract is centrifuged and microspheres on the surface removed for examination as previously described. The initial organic extract is removed and a second extraction performed to ensure complete removal of the hydrocarbon phase. The extracts are combined and filtered through a 45 micron filter to remove suspended particulates. The extract is evaporated to a small volume by warming in a water bath and the residual oil/wax examined by high temperature gas chromatography. Although useful for sample comparisons, the value of characterization of the oil or wax as indicative of a particular producer is unknown because material from different suppliers may be used by a single emulsion producer [23] and a number of different trade named oils have been mentioned in the patents issued on these materials.

The residue remaining after the organic extraction is dried, then extracted with hot water. Aluminum granules remain after hot water extraction and are identified using instrumental or chemical tests. The aqueous extract is tested for NH_4^+ , Na^+ , Ca^{++} , Cl^- and NO_3^- using

the chemical and instrumental tests previously described. In addition, spot or crystal tests for perchlorates using methylene blue/ ZnSO_4 , triphenylselenium chloride or tetrabutyl ammonium chloride should be conducted to identify this sensitizer, if present. Depending on concentration, a lavender precipitate or violet needles are formed with methylene blue, a white precipitate or white needles in clusters with triphenyl selenium chloride and tetrabutyl ammonium chloride forms a white precipitate or small crystals resembling chips of glass. Alternatively, IC for anions and cations can be used. Although amine-type chemical sensitizers are infrequent in emulsions, one which has been used in some formulations is ethylenediamine dinitrate. Formation of a complex with zinc permits determination of ethylenediamine by IC at levels of about 1 ppm without interference from other monovalent cations and amines [24].

Conclusion

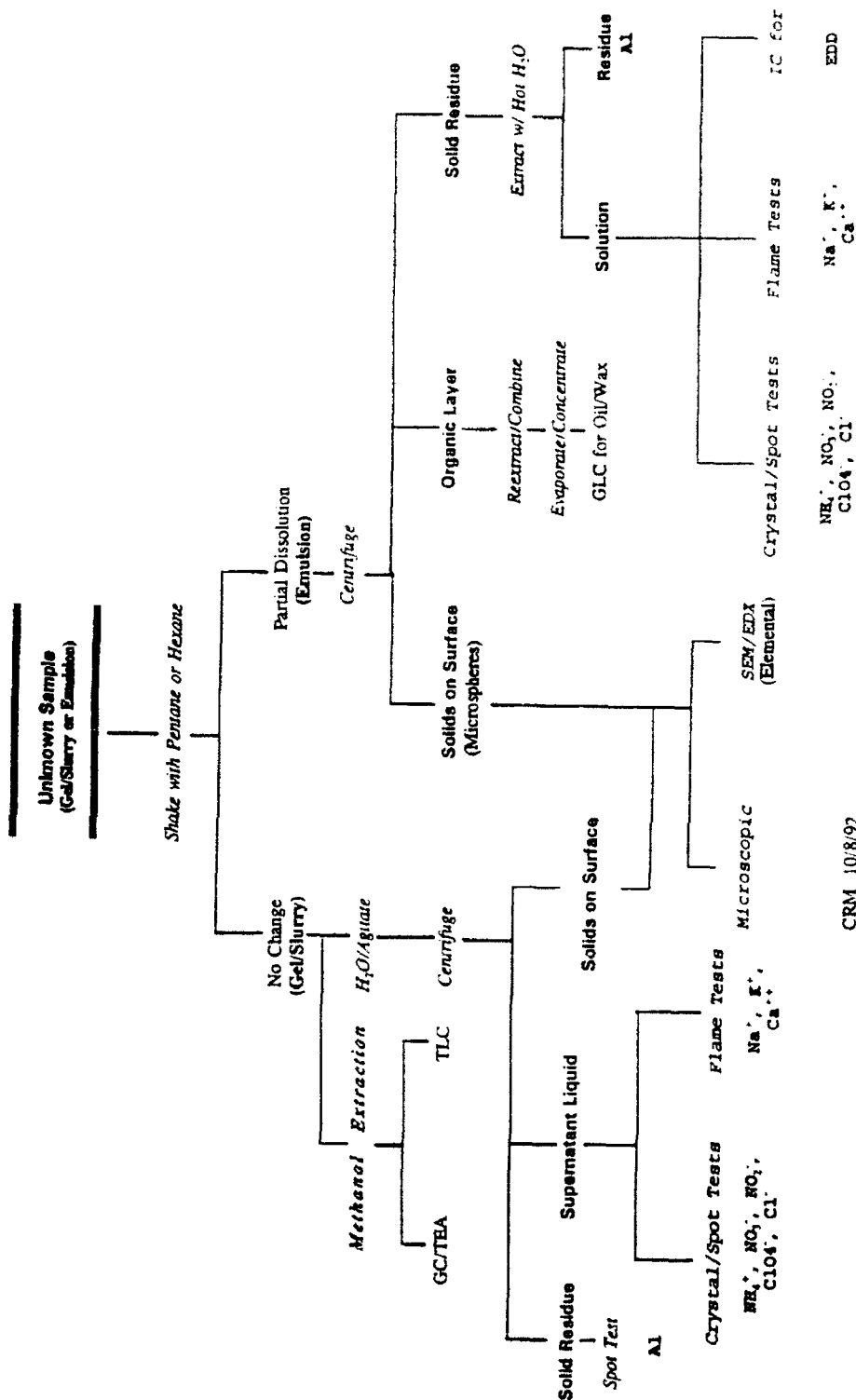
Cap-sensitive gels, slurries and emulsions are rapidly replacing more traditional commercial explosives. They are increasingly becoming available to, and employed by, terrorists and criminals. Identification and characterization of these explosives by the laboratory is essential to effectively assist in the investigation and prosecution of bombing incidents.

The following flow chart is an expanded version of an analytical scheme for the examination of slurry and emulsion explosives [25]. Using a series of relatively simple chemical and instrumental tests, samples of only a few grams of an intact slurry or emulsion explosive can be identified by type and characterized to the extent required. With a systematic approach, these explosives, new tools for terrorists, become less of a challenge for identification and characterization in the forensic laboratory.

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Analytical Scheme



CRM 10/8/92

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THE WORK OF THE EXPLOSIVES & GUNSHOT RESIDUES UNIT OF THE FORENSIC SCIENCE SERVICE (UK)

R M KING
Forensic Science Service
Priory House, Gooch Street North
Birmingham, B5 6QQ
United Kingdom

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ABSTRACT. Explosives and gunshot residues trace analysis has been centralised in a purpose-built facility at the Birmingham Forensic Science Laboratory. A combined swabbing kit has been designed to recover

explosives and gunshot residues from skin surfaces and hair. Clothing is examined by vacuum filtration onto membrane filters. Samples are cleaned-up in a micro-column procedure. Most of the major components of explosives and ammunition propellants may be detected sensitively and with substantial specificity by high-performance liquid chromatography with amperometric detection at a mercury drop electrode. For confirmation of their identities the HPLC peaks are trapped out and examined by gas chromatography with a Thermoelectron TEA detector. Ammunition primer particles are detected by scanning electron microscopy with X-ray analysis. Examples of the application of the techniques in casework are presented.

1. Introduction

In 1983 Dr John Lloyd presented a paper to the 1st International Symposium on the Analysis and Detection of Explosives, describing his work using High Performance Liquid Chromatography with a Pendant Mercury Drop Electrode detector (HPLC-PMDE) for explosives analysis. The aim of my lecture today is to describe how the work pioneered by Dr Lloyd has produced significant improvements in the analytical service that can be offered to the Police and Courts in those criminal cases in which guns or explosives are used.

I have arranged my lecture in three parts. First I will outline how the Explosives and Gunshot Residues Unit of the Forensic Science Service (FSS) came into being. Secondly, I will describe the methods we use to recover and analyse casework material. Finally, I will show what has been achieved by using these methods in casework and what needs to be done to overcome the problems that remain.

2. History

The Forensic Science Service consists of six regional laboratories in England and Wales. Until a few years ago each of these laboratories would examine items for explosives traces or gunshot residues. However, because fortunately, crimes involving explosives and guns were still relatively rare in most regions of the country, each laboratory would only see a handful of these sorts of cases each year. It was difficult in these circumstances, to build and maintain expertise.

At that time gas chromatography (GC) with electron capture detection was the principal method used for identifying explosives traces. It was a sensitive but not very specific technique.

Gunshot residues were detected by using the scanning electron microscope with energy dispersive X-ray analysis (SEM-EDX) to search for ammunition primer particles. Searching was done manually and was very time-consuming and tiring for the operator. A typical shooting case would tie up the SEM for days on end, with consequent delays to the many other types of cases which required elemental analysis.

Meanwhile, Dr John Lloyd was developing a method for detecting explosives compounds by HPLC with amperometric detection. As a result of the work a decision was made to regionalise explosives analysis at three of the six FSS laboratories. Shooting cases would still however, be examined by SEM-EDX at each of the six laboratories.

Experiences in 1985 suggested that despite regionalisation of the work, there were still problems in developing sufficient expertise in explosives analysis. Finally, the decision was made to centralise all explosives and gunshot residues work submitted to the FSS from the 41 provincial police forces in England and Wales in a purpose-built facility at the Birmingham laboratory.

The Explosives and Gunshot Residues Unit occupies an area of approximately 85 square metres on the second floor of the Birmingham laboratory. It is equipped with 2 HPLC-PMDE rigs, a GC with a Thermoelectron Model 610 Nitrogen Detector (TEA) and a Camscan Series II Electron Microscope with an automated stage driven by a Link AN10000 EDX system. The Unit is staffed by 2 Court Reporting Officers, an SEM operator and an assistant scientist.

3. Methods

3.1 RECOVERY

When a gun is fired traces of material from the ammunition may be deposited on the skin and clothing of the firer. This material is called gunshot residue. It contains components from the bullet, cartridge case, propellant and primer. In particular, the traces of unburnt propellant may contain explosives compounds such as nitroglycerin

and 2,4-dinitrotoluene. Similarly, if a person handles explosives then traces of the explosives will be transferred to his skin, clothing and other belongings.

These traces of explosives or gunshot residues can be recovered from the skin by a Swabbing Kit which we have developed at the Birmingham laboratory and which is now issued to all the provincial police forces in England and Wales.

The Kit contains non-woven cotton cloth swabs pre-wetted with a mixed solvent of 80% isopropanol and 20% water and sealed in foil packets. The swabs are used to sample the hands, face and neck of the suspect. In addition, there is a nail scraper and a swab threaded through a comb to sample the hair.

The Kit has been well received by users because it is much easier to employ than its predecessors. It has the added advantage that the swabs are processed at the laboratory in the tubes in which they are returned by the Police. There are therefore none of the problems involved in the transfer of swabs and extracts between containers.

The Kit will recover gunshot residues as well as explosives and could in principle be applied to recover any trace material that can be taken into solution.

Clothing and other items are sampled by vacuum filtration onto 1 micron membrane filters with the membrane support section of a Swinnex filter used as a coarse filter at the intake. The advantage of this filter assembly is that it is disposable so there is no danger of contaminating items with material from an earlier case. The filters are steeped then extracted with acetonitrile at the centrifuge to recover any explosives traces.

3.2 ANALYSIS

3.2.1 HPLC-PMDE. For the highest sensitivity and specificity and to maintain a good standard of instrument performance, sample extracts are routinely cleaned-up by solid-phase extraction in a micro-column procedure using Chromosorb 104 as adsorbent. The samples are then screened for explosives by HPLC-PMDE. (TABLE 1).

On leaving the HPLC column each of the compounds that made up the sample enter, in turn, the amperometric detector. Here the compounds impinge on a pendant mercury drop electrode held at a potential of -1V. Any explosives in the sample are detected by the electrochemical current produced when they are reduced at the mercury electrode. Most of the non-explosives compounds that occur in samples are not reduced at the mercury electrode and do not produce a signal from the detector.

It is possible that a non-explosive compound could give a peak corresponding in retention time to an explosive, and this does occur from time to time. However, the advantage of the amperometric detector is that by varying the electrical potential of the detector it is possible to check whether a peak is likely to be due to an explosive or not.

For example, the voltammograms of RDX, nitroglycerin and TNT differ considerably between one another. All three compounds are detected equally well at high negative potentials. But at low potentials, below about -0.2V, only TNT gives a significant response and could therefore be detected exclusively of the other two compounds. Similarly nitroglycerin could be detected exclusively of RDX. Hence the potential of the mercury electrode can be varied to characterise individual compounds. What this means in practice is that if, for example, a sample contains a peak corresponding in retention time to nitroglycerin, then the identity of the peak can be checked by changing the potential of the electrode and comparing how the size of the peak changes relative to a known sample of nitroglycerin. If the questioned peak does not change by the same proportion then it is not nitroglycerin.

3.2.2 Peak Trapping & GC-TEA. Altering the potential of the HPLC detector is not the main method of confirming the identity of a peak, although it does help to rule out several possible interfering compounds. In order to properly confirm the identity of a peak from the HPLC, it is trapped from the chromatography effluent onto a microcolumn of porous polymer using a 4-way valve situated between the end of the chromatography column and the detector. The trapped HPLC peak is washed from the microcolumn and then injected onto a gas chromatograph with a Thermo Electron TEA detector. (TABLE 2).

Compounds eluting from the gas chromatograph enter a catalytic pyrolyser. Nitrated organic compounds such as explosives generate nitric oxide which reacts with ozone generated within the TEA to give nitrogen dioxide in an electronically excited state. The excited nitrogen dioxide decays back to the ground state with the emission of characteristic radiation in the red and infra-red region of the spectrum. The emission of radiation is detected by a sensitive photomultiplier and the associated electronics amplify this signal to produce a response on a recorder.

The combination of trapping and two uncorrelated analytical techniques is a reliable method of identifying explosives traces and minimises any question of whether the confirmatory technique is responding to the relevant compound. The limit of detection of the combined techniques corresponds to around 1 nanogram of explosive on a hand swab.

3.2.3 SEM-EDX. The Swabbing Kit and vacuuming procedure described earlier will also recover the inorganic components of gunshot residue. These include the characteristic particles containing lead, barium and antimony, which are derived from modern ammunition primer.

The inorganic components of gunshot residue are detected by SEM-EDX. The particles mostly contain elements with a high atomic number. They appear as bright features against a dark background when viewed with the back-scatter detector of the SEM. The X-ray analyser of the SEM is used to automatically detect a bright particle in a sample and to collect its X-ray spectrum. The spectrum is then compared with standard spectra stored in the analyser to determine if the composition of the particle is characteristic of gunshot residue.

The Unit has an automatic SEM, dedicated to search for inorganic gunshot residue particles. This means that shooting cases no longer delay the other types of cases that need analysis and the SEM operator is no longer involved in a tiring and time consuming examination.

4. Casework Experience

Before the work was centralised at the Unit the FSS was examining around 20 explosives cases and 30 gunshot residues cases in a year. Last year the Unit examined 27 explosives cases and 91 gunshot residues cases. This suggests there was a considerable latent demand for gunshot residues work which has now been addressed with the formation of the Unit.

The success rate in gunshot residue cases before the work was centralised and propellant analysis was introduced, was around 10%. Of the 91 shooting cases that were examined in the Unit last year, propellant was detected in 33% of them. (TABLE 3).

More than half of the cases examined involved shotguns. The success rate (37%) from these cases involving shotguns was only slightly less than that from cases involving other types of gun (40%).

Ammunition primer particles were only detected in 1 case. However, cases were usually only examined for primer particles if no propellant was detected.

On average, 9 ng of nitroglycerin was detected on positive Swabbing Kits and 42 ng on positive clothing (TABLE 4). When 2,4-dinitrotoluene was detected it was present in smaller amounts. This reflects the fact that most propellants contain larger amounts of nitroglycerin than 2,4-dinitrotoluene.

The average time between the shooting incident and samples being taken was 8 hours for positive Swabbing Kits and 20 hours for positive clothing samples.

Explosives traces were detected in only 6 of the 27 cases examined. (TABLE 5).

It takes around 1 hour to examine an item of clothing for propellant or explosives traces. A Swabbing Kit takes around 3 hours. The SEM automatic search routine takes about 3 hours to search the debris collected from one item.

The HPLC-PMDE is a robust method which needs very little maintenance and gives many months of trouble-free operation. This contrasts with the behaviour of the GC-TEA. The performance of the GC-TEA quickly deteriorates, even with the clean samples trapped from the HPLC. In order to counter this deterioration and to allow larger volumes of sample to be injected onto the GC column, a retention gap is used. Even so, we find that we have to replace the retention gap after nearly every case, in order to maintain the performance of the system.

The HPLC-PMDE method cannot be applied to cases involving single base propellants which contain nitrocellulose alone. Nitrocellulose can be detected using Size Exclusion Chromatography but it is of little evidential value since it is used in many other materials besides ammunition propellant. It may be possible to detect some of the additives such as centralites, which are present in propellants. However, this would require an order of magnitude improvement in the sensitivity of the analytical methods, because these additives are only present in very small amounts in the original propellant.

Work is underway in the Unit to improve on the TEA as a method of confirmation of identity. The ideal method of confirmation would be a full mass spectrum of any peaks of interest from the HPLC. This is not yet possible for the very small amounts of material that are usually found in casework.

5. Conclusion

Considerable improvements have been made in the analytical service provided by the Forensic Science Service for the detection of explosives and gunshot residues traces. These improvements have resulted from centralising the work in one laboratory and applying improved methods of analysis.

Casework samples are screened for organic explosives or ammunition propellant by high performance liquid chromatography with amperometric detection at a mercury drop electrode. Peaks of interest are trapped from the HPLC and their identities are confirmed by gas chromatography with a TEA detector. If necessary, inorganic gunshot residues can also be detected, using an automated scanning electron microscope with an energy dispersive X-ray analyser.

Using these methods the number of cases examined for gunshot residues has increased by a factor of three and the success rate has increased from one in ten cases to one in three.

6. References

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Wolten G M, Nesbitt R S, Calloway A R, Loper G L, Jones P F (1977) 'Final Report on Particles Analysis for Gunshot Residue Detection', Aerospace Report No ATR-77 (7915)-3, 1-196

TABLE 1. HPLC Conditions

Column:	ODS, 5 micron, 150 x 4.5 mm., @ 40 deg. C
Eluent:	Aqueous phosphate (0.035M, pH3) methanol, 89:100, 1 ml/min.
Detector:	Pendent mercury drop electrode (L drop) at -1V. vs Ag/AgCl.
Sample Loop:	10 microlitres

TABLE 2. GC-TEA Conditions

Column:	2 m x 0.32 mm Silica Retention Gap + 5 m x 0.32 mm SE52/4, 0.5 micron
Carrier Gas:	Helium, 1 kg / cm ²
Injector:	Air-cooled on-column
Temperature Programme:	60°C then 25°C/min to 230°C
Detector:	Thermoelectron TEA, interface 250°C, pyrolyser 850°C

TABLE 3. Gunshot Residue Cases April 1991-April 1992. Results and types of gun used

	Total Cases	Propellant Detected	Primer Detected*
Shotguns	49	18	0
Others	25	10	1
Unknown	17	2	0
	91	30	1

* Cases examined for primer if no propellant detected.

TABLE 4. Gunshot Residues Cases April 1991-April 1992. Amounts and time intervals

	Swab Kits		Clothing	
	Mean	(Range)	Mean	(Range)
Nitroglycerin	9 ng	(5-17)	42 ng	(4-266)
2,4-Dinitrotoluene	3 ng	(2-3)	8 ng	(2-12)
Incident-Sampling Interval	8 hrs	(3-19)	20 hrs	(3-96)

TABLE 5. Explosives Cases April 1991-April 1992

Explosive	No of Cases
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Nitroglycerin	1
RDX	2
TNT	1
Sugar/Chlorate	1
Flash Powder	1
None Detected	21

Total	27
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ANALYSIS OF ORGANIC GUNSHOT RESIDUES

C. E. CORLESS

*Metropolitan Police
Forensic Science Laboratory
109 Lambeth Road
London
SE1 7LP
U.K.*

ABSTRACT. A comparison was made of chromatographic parameters for gas and high performance liquid chromatography methods employed in the analysis of organic gun shot residues. A solid phase extraction procedure was adopted to provide sequential analysis of swabs or filters. The analytical procedure was tested using swabs from gun barrels and filters from vacuum clothing samples with particular reference to the reliability of quantification.

1. Introduction

At The Metropolitan Police Forensic Science Laboratory, gunshot residues (GSR) are routinely analysed by Scanning Electron Microscopy/Energy Dispersive X-Ray Analysis (SEM/EDX). This technique looks for the characteristic three element particle (lead, antimony and barium) or indicative inorganic particles resulting from primer residues. Currently a number of brands of ammunition do not have a primer composition with all the elements needed for 'unique' primer GSR determination. Indeed there is also on the market an organic based primer, SINTOX, which has no antimony, lead or barium. In the future the importance of a GSR identification method based on organic analysis may therefore be raised. This paper outlines the current methods used at MPFSL for organic GSR identification with particular reference to the reliability of quantification. The solid phase extraction procedure adopted is an amalgamation of two previous methods by Lloyd [1] for HPLC and Douse [2] for GC.

2. Materials and Methods

2.1. MATERIALS

The analysis of organic GSR has mainly focused on Nitroglycerine (NG) with 2,4-Dinitrotoluene (DNT) included as a possible component of the ammunition used in this study. NG and Butane-1,2,4-triol trinitrate (BTN) were donated by RARDE, Sevenoaks, U.K. DNT and 4-Nitrotoluene (NT) were bought from Aldrich, Gillingham, U.K. Musk Tibertine (MT) was a gift from

Givaudin, Whyteleafe, U.K.

HPLC (Acetonitrile, Methanol) and Distol (Pentane, Ethyl Acetate) grade solvents were obtained from Fisons, Loughborough U.K. Methyl *tert*-butyl ether was obtained from Rathburns, Waterburn, U.K. and Isopropanol from Rhone Poulenc, Manchester, U.K. All were used without further purification.

Ethafoam expanded polyethylene foam was purchased from Foam Engineers, High Wycombe, U.K. Amberlite XAD7 and 4 resins of analytical grade with 0.1 - 0.2mm and 0.3 - 1.0mm particle size respectively were purchased from Universal Biologicals, London, U.K. Chromosorb 104, 100 - 200 mesh size was bought from Phase Separations, Queensferry, U.K. Water was purified through a Milli-RO6 and -Qplus system (Millipore, Harrow, U.K.)

2.2. SWABBING OF GUN BARRELS

Litex 10, a non woven cloth from LIC CARE, Farnborough, U.K. was used to swab gun barrels both before and after firing. The swabs were soaked in approximately 1ml of isopropanol/water (8/2 v/v). Three SMITH AND WESSON model 10 handguns were used. The ammunition chosen was WINCHESTER SUPER-X 0.38 SPECIAL 158GR with lead bullet, a known double based propellant analysed to contain approx. 26g NG.100g⁻¹ of propellant but no DNT. One swab was used to sample the inner and outer gun barrel (BG) prior to firing the gun once with a full load. Swabs were then taken after firing of both the inner (GI) and outer barrel (GO). All appropriate blanks and controls were taken.

2.3. VACUUM SAMPLES FROM CLOTHING

Clothing was vacuum sampled using a glass fibre disc (AP40 Prefilter Millipore, Harrow, U.K.) in a 2ml glass Luer syringe barrel (Chance Brothers, Malvern Link, U.K.) connected to a vacuum line by the syringe Luer fitting. The syringe was then held in the centrifuge tube by cutting a hole in the lid to fit the barrel diameter. Two samples per garment were taken, one to act as a blank and one to be spiked with 87ng of NG prior to extraction and analysis. The three clothing samples C1 outdoor jacket, C2 towel (skin debris) and C3 jumper were sampled together with a procedural blank F1.

2.4. SOLID PHASE EXTRACTION COLUMNS

Standard stock solutions of the explosives were diluted to approx. 1mg.ml⁻¹ in either ethyl acetate, acetonitrile or acetone and spiked where necessary onto swabs, filters or into 1ml isopropanol/water (8/2 v/v) solution prior to extraction.

Two types of columns were used, either 25cm x 2.5mm ID silanised glass columns or 1ml disposable syringes (Merck Ltd, Lutterworth, U.K.). The glass columns were packed with absorbent resins, column bed height 2cm (XAD 7) or 3cm (Chromosorb 104/XAD4), between two ethafoam plugs. The disposable syringes were filled up to 0.1ml mark giving a column bed height of 15mm. The resins were prepared for use by washing through a bed of resin with a number of solvents, non-polar through to polar, followed by drying at 120°C (XAD resins) or 80°C (Chromosorb 104) for 2 to 3 hours. The resins were cooled to room temperature and stored in the appropriate solvent.

After sampling (sections 2.2+2.3) the internal standard BTN was added to the swab or filter, which was then centrifuged at 3000 rev.min⁻¹. Water (1ml) was added to the swab or filter before being centrifuged for a second time under the same conditions, in order to improve the

absorption of the more polar compounds such as nitrate esters on the solid phase resin. The resulting solution was transferred to a Chromosorb 104/XAD4 mixed bed column which had been prewashed with acetonitrile and isopropanol/water (8/2 v/v). The column was eluted with 250 μ l of acetonitrile. 100 μ l of the acetonitrile extract was transferred to an XAD7 column which had been prewashed with ethyl acetate, pentane and acetonitrile. 0.3 μ l of NT stock solution was added to remainder of acetonitrile extract. The XAD7 column was washed with 500 μ l of pentane or pentane/methyl *tert*-butyl ether prior to elution with 400 μ l of ethyl acetate. 0.8 μ l of MT stock solution was added to the ethyl acetate extract. NT and MT were added to HPLC and GC extracts prior to injection to act as internal standards in order to correct for fluctuations in the final volume.

2.5. CAPILLARY GAS CHROMATOGRAPHY (GC)

Two GC systems were set up: one using electron capture (Carlo Erba Ni⁶³ ECD 40) the other chemiluminescence (Thermal Energy Analyser TEA from Thermo Electron Model 610) detection. The GC used were Carlo Erba Model 4130 and HRGC respectively. Operating conditions were as follows: ECD - Injector on column OCI-3 (SGE Milton Keynes U.K.). Column Rt_{ss} fused silica capillary 7.5m x 0.25mmID (Restek Thames Chromatography, Maidenhead, U.K.) and 5m x 0.35mmID phenyl methyl deactivated retention gap, stationary phase thickness 0.25 μ m; Temperature programme 70°C initial temperature then 20°C.min⁻¹ to 205°C held 4min; Carrier gas helium, flow rate 1.3 ml.min⁻¹ with 5% methane in argon 40ml.min⁻¹ as makeup gas; Detector temperature 210°C. TEA - as for ECD except on column injector part of GC; final temperature in temperature programme 230°C; Pyrolyser temperature 725°C; carrier helium 1.3ml.min⁻¹; TEA reaction chamber pressure 0.3 - 0.4 mmHg.

2.6. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

HPLC was used under reverse phase conditions using a 15cm x 4.6mm ID analytical column (Capital HPLC Specialists, Bathgate, U.K.) with a 1cm guard column both packed with 3 μ m Hypersil ODS. The pump used was an isocratic pump from ACS Macclesfield, U.K. model 351. The detector employed was a static mercury dropping electrode (SMDE) model 303 from EG&G Instruments, Wokingham, U.K. with a model 174A polarographic analyser also from EG&G. Operating conditions were as follows: eluent 65/100 phosphate buffer (0.025M pH3)/methanol degassed by bubbling nitrogen through solution under gentle reflux; column heater 40°C; flow rate 0.7 ml.min⁻¹; injection volume 10 μ l, sample diluted at least three times and degassed through injection port for at least two min.; detector hanging mercury dropping electrode mode, 1 large drop per chromatogram, eluent line to drop distance 0.45mm; polarographic analyser DC mode held at -1.0V vs Ag/AgCl reference electrode.

3. Results and Discussion

3.1. COMPARISON OF GC AND HPLC METHODS

A brief comparison of the chromatographic characteristics of the GC and HPLC systems was conducted (Table 1). Retention time (Rt) reproducibility of approx. 2% was found for all three systems. The HPLC eluent was under reflux, which could have led to difficulties with Rt reproducibility. However, with care, reproducibility similar to capillary GC can be achieved and

maintained. A difference in peak height reproducibility was evident. Long term reproducibility was defined as relative standard deviation (RSD) produced from repeated injection of a standard (total $n=10$ injections) over 70 other injections of sample extracts and standards. The value obtained for HPLC analysis is acceptable. However the GC values of approx 30% NG for both ECD and TEA represent a difficulty which could cause quantification problems. The high RSD is observed as a loss of detector response with time. As this is independent of detector, the cause of this decay must be chromatographic. This agrees with information on nitrate ester decomposition when dirty samples are injected resulting in a rapid fall in detector response. As BTN also decays in a similar fashion it is possible to make a recovery correction and maintain quantification. The limit of detection calculated were similar to those previously reported.

TABLE 1. Comparison of HPLC and GC methods

%REPRODUCIBILITY	ECD	TEA	HPLC
Retention time (min)		1.6	2.6 1.9
Peak height NG/BTN (mm) long term $n=10$	28/19	34/30	9/7
Limit of detection pg on column 3 x signal/noise ratio	9	9	19

3.2. SOLID PHASE EXTRACTION PROCEDURE

If BTN is to be used as an internal standard the recovery values must be the same or near to that of NG. A mixed bed of Chromosorb 104 and XAD7 was employed to extract the nitrate esters for HPLC analysis as described by Lloyd [1]. These absorbants were packed to produce columns through which extract is washed, hopefully retaining the compounds of interest and either strongly retaining or losing the non-retained unwanted material. Chromosorb 104 is an acrylonitrile co-polymer and is used mainly to trap polar compounds whilst non-polar compounds are trapped by XAD4. Therefore the combination should produce the desired result, Lloyd was able to recover approximately 70% NG using his protocol. Set 1 Table 2 are the recovery values using glass columns and spiked solutions. A recovery of 50%+ was achieved for both NG and BTN. However with syringe barrels and swabs / filters the results were more variable (Set 2 Table 2). Although with practice, good recovery was obtained with approximately 70% recovery for both NG and BTN Set 3 Table 2.

TABLE 2. Percentage recovery of NG and BTN from CHROMOSORB 104 / XAD4 columns.

SET	SPIKE NG ng	% RECOVERY	
		NG	BTN
1	52	50	59
2 SWAB	12	72	41
	60	40	44
FILTER	12	56	40
	60	34	49
3 FILTER	87	69	73

The original solvents used by Douse in his protocol unfortunately gave higher recovery for BTN than NG (set 1 Table 3) thus ruling out extraction for GC before HPLC. The recovery value for NG is in agreement with previously published values [3]. The use of acetonitrile as the eluting solvent for HPLC also causes problems as XAD7 does not retain nitrate esters very well from this solvent. As acetonitrile may contain traces of water which would be ruinous for a GC column, direct injection of acetonitrile was therefore ruled out. Improvement in nitrate ester adsorption was therefore required, this was achieved by reducing the polarity of the acetonitrile by addition to the column of the acetonitrile extract in a mixture of pentane or methyl *tert*-butyl ether/pentane. Set 2 Table 3 shows the recovery achieved using glass columns and spiked solutions. Slight increase in polarity, by increasing the percentage of methyl *tert*-butyl ether, shows dramatic reduction in recovery thereby confirming that solvent polarity was the limiting factor. By using pentane, NG was recovered at least to approximately Lloyd system levels. Unfortunately BTN is very poorly recovered. As 25% methyl *tert*-butyl ether/pentane mix does produce admittedly poor, but similar recovery this was used for the gun swabs. Increasing the amount of XAD7 by using syringe barrels improved the recovery of BTN giving approximately 45% for both NG and BTN. This was therefore utilised for the clothing vacuum samples.

TABLE 3. Percentage recovery of NG and BTN from XAD7 resin columns.

SET	SPIKE NG ng	% RECOVERY		NOTES
		NG	BTN	
1	10	43	76	Lloyd [3]
2	196	40	14	Pentane*
	196	12	13	25% MtBE/Pentane*
	196	6	3	50% MtBE/Pentane*
3	230	45	44	Pentane* SYRINGE
	230	25	17	Pentane* GLASS

* mixed with acetonitrile extract

MtBE - Methyl *tert*-butyl ether

3.3. TESTING OF SOLID PHASE EXTRACTION PROCEDURE

TABLE 4. NG from gun barrel tests (ng per swab).

SWAB	ECD		TEA		HPLC	
	A	B	A	B	A	B
BG1	5	77	-	-	45	60
BG2	11	125	-	-	124	153
BG3	84	906	52	559	652	972
GO1	38	383	37	342	358	403
GO2	20	307	35	236	226	316
GO3	354	5.8 μ g	298	4.9 μ g	1.6 μ g	5.4 μ g
GI1	1.1 μ g		600		12.3 μ g	
GI2	1.4 μ g		600		3.9 μ g	
GI3	-		-		6.4 μ g	

A uncorrected for recovery, B corrected for recovery

BG gun swab taken before firing

GO gun swab outer barrel after firing

GI gun swab inner barrel taken after firing.

Two simple tests were devised to test the use of BTN as internal standard and more importantly the variability between the three systems with respect to quantification. Firstly a set of swabs from gun barrels was produced (section 2.2). Table 4 gives the results of the analysis and quantification. Column A lists the ng of NG per swab recovered, corrected only by volume. The GC values are only approximately 10% of the HPLC value which is accounted for by the great difference between the GC and HPLC recoveries (GC BTN 6 - 10% HPLC BTN 70 - 80%).

However once both sets have been corrected for recovery by BTN ratios (column B Table 4) remarkably good agreement can be achieved between the systems (8 -15% RSD Table 5). GI could not be recovery corrected as the extract had to be diluted to achieve even this level of quantification thus diluting out BTN. Blank guns were cleaned before pre-firing swabbing but were shown to contain quite high quantities of NG and in one case DNT also.

Table 5. NG average value from GC and HPLC analysis (ng per swab average).

SWAB	AVE.*	RSD%
BG1	69	-
BG2	139	-
BG3	812	27
GO1	376	8
GO2	286	15
GO3	5.4 μ g	8

* average of corrected (column B) values in Table 4.

The next test was to increase the potential interferences present in the sample via clothing debris. Three types of clothing were sampled and spiked with 87ng of NG (section 2.3). Once again extracts analysed by HPLC were well recovered (70%), and when recovery-corrected, gave 95% of the spiked NG (Table 6) thereby increasing confidence in the overall accuracy of the procedure. The GC values however gave problems. Recovery of BTN was reduced to approximately 15% from 40% + of XAD7 test (section 3.2). When NG was BTN ratio-corrected, 80% + of the true NG spike was accounted for. The problem was probably related to GC decay as outlined in section 3.1. The initial XAD7 tests were carried out at the beginning of a column lifetime and the clothing samples were injected towards the end. The TEA system also suffered from the same problem.

TABLE 6. NG recovered from spiked clothing samples (ng per filter)

CLOTHING SAMPLE	HPLC-SMDE		GC-ECD	
	A	B	A	B
C1	48	81	8	68
C2	65	84	12	76
C3	55	83	-	-
F1	71	80	-	-

A ng NG on filter uncorrected for recovery

B ng NG on filter corrected for recovery

4. Conclusions.

The brief comparisons reported here of the HPLC and GC techniques would on initial view lead to the conclusions that HPLC provides a far more reliable method. However GC should not be rejected. Judicious use of internal standards means that with care the GC with either ECD or TEA could provide a useful second quantifiable method.

5. References.

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GSR PARTICLES FORMED BY USING AMMUNITION THAT HAVE MERCURY FULMINATE BASED PRIMERS

ARIE ZEICHNER and NADAV LEVIN,
Toolmarks and Materials Laboratory, Division of
Identification and Forensic Science, Israel Police
Headquarters, Jerusalem 91906, ISRAEL, and
MICHAEL DVORACHEK, Geological Survey of Israel, 30 Malkhe
Ysrael Street, Jerusalem 95501, ISRAEL.

ABSTRACT. Ammunition having mercury fulminate based primers are commonly manufactured by Eastern Bloc countries and extensively used in the Middle East. GSR particles formed by firing these types of ammunition were examined. It was observed that much lower percentage of mercury-containing GSR particles were found in samples taken from a shooter as compared to the percentage of such particles in samples from cartridge cases. This fact must therefore be taken into account when interpreting case results. A plausible explanation for the above results is proposed.

1. INTRODUCTION

The purpose of this work is to report on the observation that when firing different types of ammunition having primers containing mercuric fulminate, a much lower percentage of mercury-containing GSR particles was found in samples taken from a shooter as compared to the percentage of such particles in samples from cartridge cases. This effect was first observed in a case of homicide which prompted us to carry out simulated test shots and other experiments to aid interpretation of the results.

2. THE CASE

At the scene of a homicide, several 7.62x39mm Russian and Egyptian cartridge cases of the type fired by an AK-47 assault rifle were found. Several hours after the incident the suspect was apprehended in his home while showering. In the courtyard, several items of clothes were burning in a fire. The police extinguished the fire with water and the wet remains of the clothes were brought to the laboratory.

3. METHODS

After drying, the clothes were sampled for particles using 3M double sided adhesive-coated aluminum stubs. SEM/EDX analyses for GSR particles were carried out by manual search using a CamScan III SEM combined with a Tracor-Northern TN 5500 EDX system

GSR particles from the cartridge cases found at the homicide scene were sampled using wood sticks and then transferred to aluminum double-sided-adhesive-coated stubs.

The composition of GSR particles from Russian and Egyptian 7.62mm ammunition was found to be similar and consisted of tin (Sn), antimony (Sb), mercury (Hg), sulfur (S), potassium (K), chlorine (Cl) and copper (Cu) accompanied by small amounts of aluminum (Al), silicon (Si), iron (Fe) and zinc (Zn) (Fig.1).

ISRAEL POLICE H.Q. TN 5400
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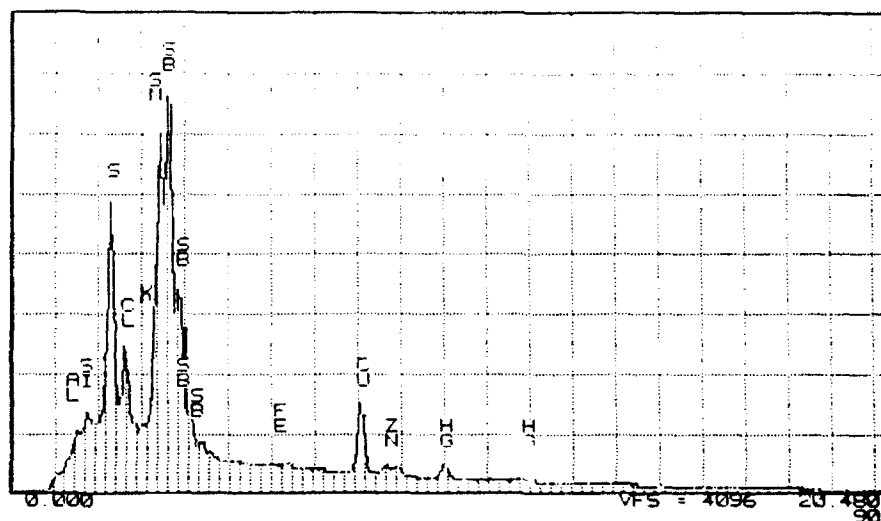


Figure 1. EDX spectrum of many GSR particles from Russian 7.62mm ammunition.

The origin of tin in these GSR particles is not from the primer mixture which consists mainly of mercury fulminate, potassium chlorate and antimony sulfide [1, 2], but from a varnished lead-tin foil disc which closes off the priming cup from the inside of the cartridge case [2].

Five GSR particles were found only in the sample taken from the partially burnt jeans. All five particles were without detectable

TII-5500 POLICE HEADQUARTER
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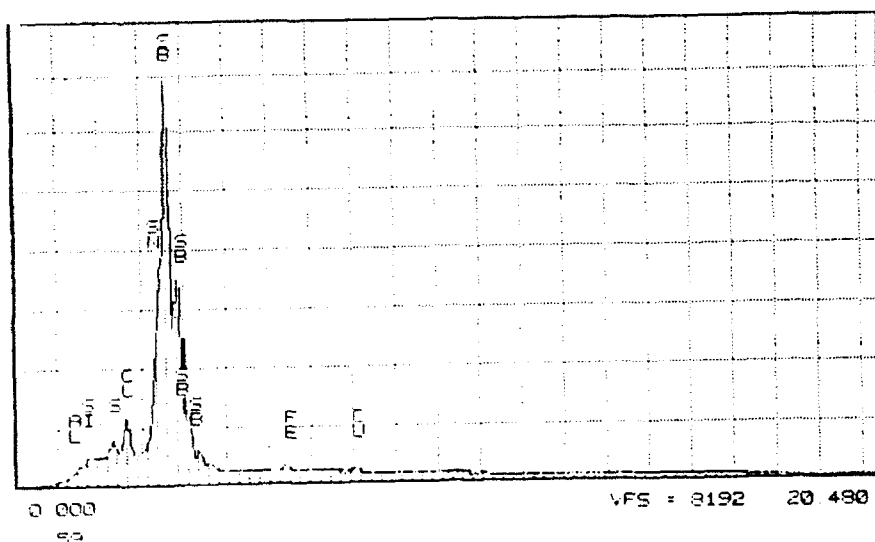


Figure 2. EDX spectrum of a typical GSR particle found in the sample from the partially burnt jeans.

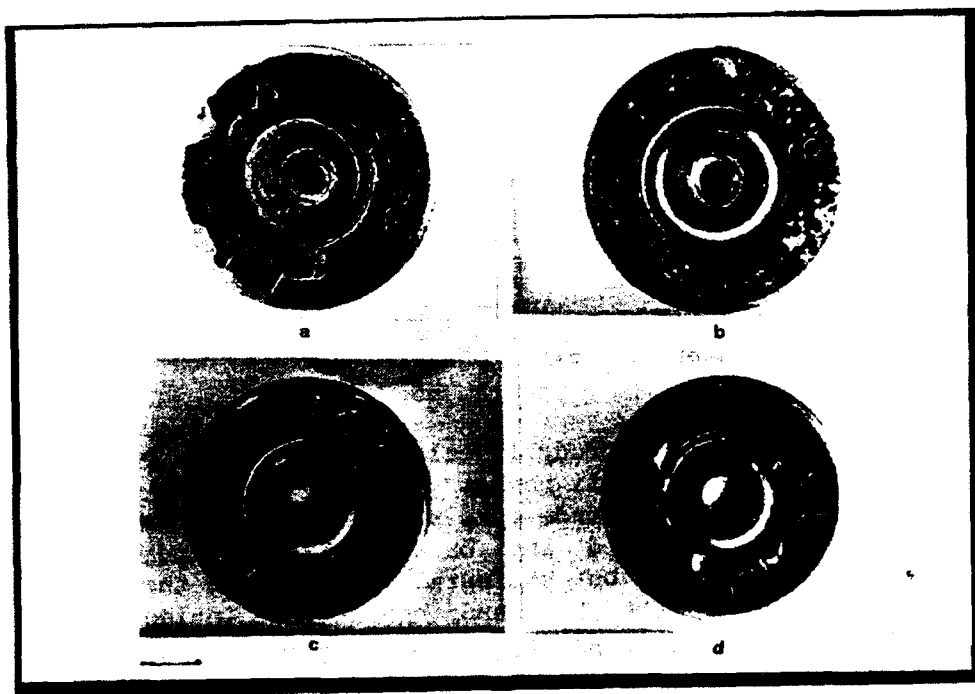


Figure 3. Fig. 3: Head stamps of the ammunition used in the shooting experiments: Egyptian 7.62mm ammunition (a), Russian 7.62mm ammunition (b), Italian 9mm ammunition (c) and Egyptian 9mm ammunition (d).

levels of mercury (Fig.2), while a large percentage of the GSR particles from the cartridge cases contained mercury. It seemed therefore, that significantly less GSR particles containing mercury may be found in the samples taken from a shooter as compared to the amount found in cartridge cases.

Shooting experiments were carried out with Egyptian and Russian 7.62mm ammunition (Fig.3 a, b) (the same types of ammunition as were found at the scene of the crime) using an AK-47 assault rifle, as well as with Italian and Egyptian 9mm Parabellum ammunition (Fig.3 c, d) using a 9mm FN semi-automatic pistol. The Egyptian 9mm and 7.62mm ammunition used had similar compositions. The composition of the Italian 9mm ammunition was different in the respect that it did not include tin (Fig.4).

ISRAEL POLICE H.O. IN 5400
Cursor: 0.000keV = 0

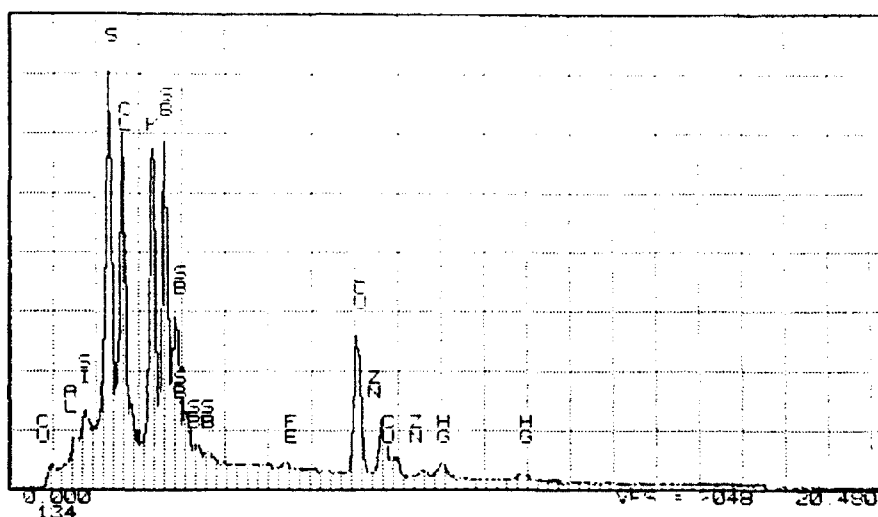


Figure 4. EDX spectrum of many GSR particles from Italian 9mm ammunition.

First, the rifle was thoroughly cleaned and a person with uncontaminated hands fired six rounds of the Egyptian ammunition. Before shooting, a hole was made in a plastic bag that was put on the rifle so that the bag covered the hands of the shooter and the discharge region of gases, but the muzzle was outside the bag. After shooting, the shooter rubbed his hands against the inside of the bag and his hands were sampled by a double-sided-adhesive-coated aluminum stub. The plastic bag was used to increase the number of GSR particles found (in order to improve statistics regarding composition), since relatively less GSR particles are found on a shooter using a rifle as compared to one using a handgun [3]. Similar tests were also conducted using the Russian 7.62mm ammunition. The shooting experiments with the 9mm handgun, were carried out in a similar way as with the assault rifle except that three rounds

instead of six rounds were fired for each ammunition type and no plastic bags were used.

SEM/EDX analysis for GSR particles in samples from the hands was carried out using an automated search system attached to a CamScan 4 SEM with a motorized stage drive and a four-sample holder combined with a Tracor Northern TN 5500 EDX system [4-6]. GSR from the cartridge cases were sampled as described above and were analysed manually.

It was reported that elemental mercury is formed in the reaction of the decomposition of mercury fulminate [1, 7]. To examine the possibility that evaporation of elemental mercury is the reason for finding much less mercury in GSR particles found on the shooter as compared to those in the cartridge cases, 7.62mm cartridge cases after first sampling were heated in the oven at 360 degrees centigrade for half an hour (b.p. of mercury is 357 degrees centigrade) and then sampled again (second sampling).

The possibility of the evaporation of mercury from particles being on the stub in the SEM (6X10 mbar vacuum) was also tested with the 9mm Egyptian ammunition. For this purpose, GSR particles from cartridge cases were sampled on the aluminum stubs coated with carbon conductive double sided adhesive tape (Structure Probe Inc., West Chester, Pa 19381 USA). Use of this tape eliminated the need to coat the stub with carbon and thus the possibility of mercury evaporation from uncoated particles could be examined. The same area (2 X 1.4mm) on the stub with many GSR particles was examined for composition immediately after the introduction of the stub into the SEM and then again 16 hours later (without the electron beam on). The same area was then kept for one hour under electron bombardment (absorbed current 1nA) and then examined for composition.

4. RESULTS AND DISCUSSION

The results of the experiments are summarized in Table 1. It can be seen that in all cases a much lower percentage of mercury-containing GSR particles was found in samples taken from a shooter as compared to the percentage of such particles in samples from cartridge cases. It can also be seen that heating the cartridge cases at 360 degrees centigrade decreased the percentage of particles containing mercury considerably. This observation supports the claim of the formation of elemental mercury in the decomposition of mercury fulminate as was reported in the literature [1, 7].

No difference in mercury content was found between the GSR particles examined in SEM/EDX immediately after introduction into the SEM and the same particles 16 hours after being in the SEM vacuum and following one hour of electron bombardment.

An explanation for the difference in mercury content between GSR particles in samples taken from a shooter and samples from cartridge cases may arise from the mechanism of GSR particles formation. As the firing pin strikes the primer housing, the primer explodes and the high temperatures obtained may vaporize the explosion products (GSR

particles). Because of supersaturation, the GSR vapors may condense back as droplets [8]. As the exploding front comprising these droplets strikes the gunpowder, they are exposed to steep rises in temperature and pressure, from the ignition of the propellant. The temperature continues to rise as the gunpowder combustion proceeds [8-10]. Therefore, GSR particles which are mixed with the burning propellant moving in the barrel and then driven out of the flash gap or ejection port, would probably experience considerably more "heat damage" than GSR particles left in the cartridge case which had effectively less "contact" with the burning gunpowder. Consequently, it would be reasonable to assume that mercury will vaporize more from GSR particles moving with the burning propellant and ejected on a shooter, than from particles left in the cartridge case.

TABLE 1. Results of Experiments with Various Types of Ammunition

Ammunition	Sample from Shooter's Hands		Sample from Cartridge Cases		Sample from Cartridge Cases, after Heating	
	N	% Hg	N	% Hg	N	% Hg
Russian, 7.62 mm	40	0	37	95	40	32
Egyptian, 7.62 mm	25	12	50	82	45	35
Egyptian, 9mm	83	11	98	100		
Italian, 9mm	28	0	75	93		

N = Number of examined particles. In the case of the Russian and Egyptian ammunition, the examined particles were those containing at least Sn and Sb. In the case of the Italian ammunition, the examined particles were those containing at least Sb and S.

% Hg = Percentage of particles containing mercury.

5. CONCLUSIONS

This study has shown that when firing ammunition which have mercury fulminate based primers, a much lower percentage of mercury-containing GSR particles are found in samples taken from the shooter as compared to the percentage of such particles in samples from cartridge cases. It is important that this is recognized by the expert when interpreting GSR case results.

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DETECTION OF TRACE EXPLOSIVE EVIDENCE BY ION MOBILITY SPECTROMETRY

Dean D. Fetterolf, Ph.D.
FBI Laboratory
Forensic Science Research Unit
FBI Academy
Quantico, VA 22135

ABSTRACT. The continuing threat of worldwide terrorism has prompted the need for new and innovative explosives detection systems. As part of an ongoing research effort, the FBI Laboratory has been evaluating new technology and the innovative adaptation of existing technology for use in counterterrorism and counternarcotics investigations. We have been examining the application of ion mobility spectrometry (IMS), for its role in explosives detection. The explosives residue is collected on a membrane filter by a special attachment on a household vacuum. Subsequent thermal desorption and analysis requires 5 seconds. Experimental results have determined the limits of detection for most common explosives to be approximately 200 pg. The persistence of explosives on hands and transfer to other surfaces has been examined. Post-blast residue of NG was detected on fragments of improvised explosive devices constructed with double-based smokeless powder. Post-blast residue from C-4, SEMTEX, and other explosives have also been detected on items of forensic and evidentiary value.

1. Introduction

Many nations, including the United States, have been prime targets of international terrorism for many years. The bombings of the U.S. Embassy and the U.S. Marine Barracks in Beirut in 1983, and the destruction of Pan American Flight 103 over Lockerbie, Scotland in December, 1988 are grim reminders of terrorism in recent years. These criminal acts have prompted the need for the development of new and innovative methods of explosives detection. As part of an ongoing research effort, the FBI Laboratory has been evaluating new technology and the innovative adaptation of existing technology for use in counterterrorism and counternarcotics investigations.

Ion mobility spectrometry (IMS) was first introduced by Cohen and Karasek in 1970 [1]. Much of the earlier work on the applications of IMS technology focused on fundamental studies and laboratory feasibility. In a recent review it was pointed out that IMS technology is experiencing a resurgence of interest in specific purpose detection systems because of its analytical flexibility [2].

We have been examining the application of IMS to explosives detection in a variety of scenarios of forensic interest by collecting the trace physical evidence transferred to hands

or surfaces through contact or post blast residue. The exceedingly low vapor pressure of explosives (ppm to ppt) [3], makes their detection by vapor methods alone difficult.

In general, IMS possess many of the desirable analytical figures of merit of conventional laboratory-based instruments such as good sensitivity, selectivity, and speed of analysis. They are often small and simple to operate. This ease of use and portability permit operation in real world scenarios not only as a forensic tool but also as an investigative tool.

The value of IMS as an investigative tool (rather than purely a laboratory tool) is exemplified in recent applications which have included the detection of drug micro-particulates on hands [4,5], determining cocaine in injection molded plastic [6,7] and use in customs scenarios [8]. Forensic applications of IMS technology from 1970 to 1989 have been thoroughly reviewed by Karpas [9]. We present here our results demonstrating the application of IMS to the detection of trace physical evidence from explosives.

1.1 TECHNIQUE

The instrument used in these experiments was the Barringer IONSCAN Model 200 (Barringer Instruments, Inc., South Plainfield, NJ). The IMS block diagram in Figure 1 consists of two main areas: the reaction region and the drift region. In the reaction region, atmospheric pressure carrier gas (purified air), hexachloroethane (C_2Cl_6), the reactant gas and 4-nitrobenzo-nitrile, an internal calibrant are ionized by a ^{63}Ni beta emitter to form Cl^- ions. The use of modified ion chemistry to improve the sensitivity and selectivity of detection by IMS is quite common. The reactant ions can then undergo one or more ion/molecule reactions with an explosive molecule. Karpas has reviewed the ionization of explosives in IMS under a variety of operating conditions [9]. In general, negative ionization provides a high degree of selectivity because only highly electronegative compounds such as explosives are ionized.

Under the influence of an electric field, the mixture of reactant and product ions reaches a shutter grid that separates the reaction region and the drift region. The shutter grid is made of sets of thin mesh wires with a voltage bias between them. When the shutter grid is "on" (with bias voltage applied), the ions are attracted to the gating grid and lose their charge. For a brief amount of time the grid is turned "off." Ions are then transmitted into the drift region of the cell. In the drift region an electric field gradient is applied. The ions migrate through the electric field, but at the same time are hindered by the countercurrent drift gas. The smaller, compact ions have a higher mobility than the heavier ions, and therefore traverse the region and collide with the electrometer plate in a shorter time. With the aid of a microprocessor, a plot of ion current intensity versus the time elapsed from the opening of the shutter grid gives the mobility spectrum or plasmagram.

1.2 THEORY

The drift velocity, v_d , (cm/s) of an ion traversing through an electric field gradient, E , (V/cm) is proportional as follows:

$$v_d = KE \quad (1)$$

where the proportionality constant, K , is the mobility of the ion in $cm^2V^{-1}s^{-1}$.

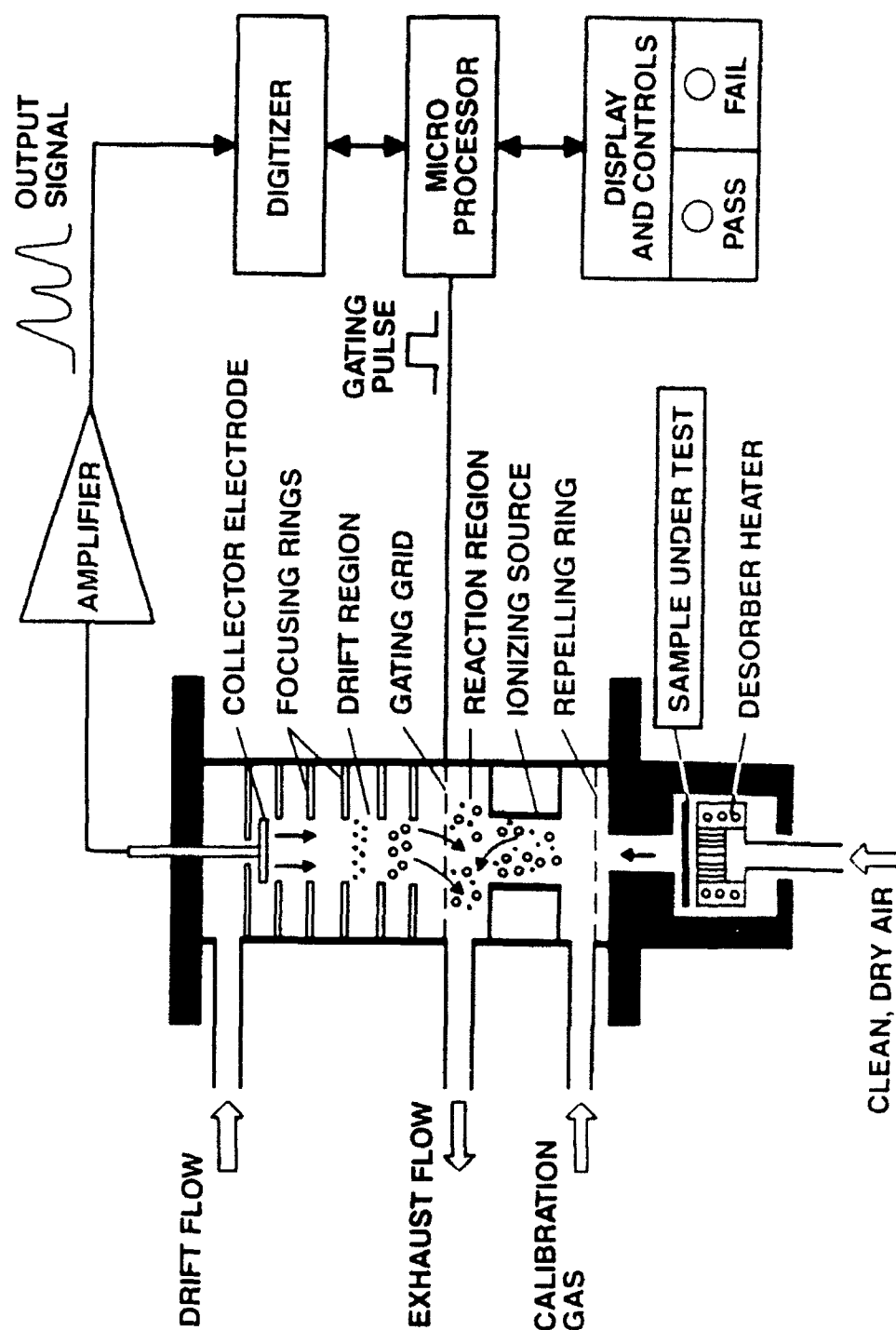


Figure 1. Block diagram of the Barringer Ionscan Model 200 Ion Mobility Spectrometer.

If t is the required time (sec) for the ion to travel the drift region length (cm), d , at this velocity, and the drift velocity is the drift length divided by the drift time, then

$$K = d/(Et) \quad (2)$$

in general, for a given temperature, T (Kelvin) of the drift gas and pressure, P (torr) the mobility is given as reduced mobility, K_0 , in the form of

$$K_0 = [d/(Et)] (273/T) (P/760) \quad (3)$$

With a given set of electric field gradient, temperature, and pressure conditions, the product of the reduced mobility and the drift time of an ion, $K_0 t$, is a constant.

From the above equation, it can be seen that the ratio of the reduced mobility of any two species is independent of operating conditions and allows for the use of the calibrant as an internal standard. The ratio of the sample ion mobility to the mobility of the calibrant corrects for any drift and provides for identification and alarm triggering. The audible IMS alarms were calibrated by analyzing standard samples of the explosives of interest.

Ion behavior can also be derived from the fundamental relationships between ion mobility and collision processes at the molecular level as expressed by McDaniel [10]:

$$K = (3e/16N)(2\pi/kT)^{1/2} \times (m + M/mM)^{1/2}(1/\Omega) \quad (4)$$

where e is the charge on the ion, N is number density of the drift gas, k is the Boltzmann's constant, T is the absolute temperature, m is the ion mass, M is the mass of the drift gas, and Ω is the average collision cross section which is determined by ion size, shape, and polarizability.

From this equation a nonlinear relationship exists between the ion mobility and mass. A semilogarithmic plot of reduced mobility vs mass should produce a straight line. Comparing equations (2) and (4) also suggests that a plot of drift time vs mass should also be linear. These relationships can be helpful in determining the mass of an unknown species in the IMS as will be demonstrated in the following section.

2. Results and Discussion

2.1 IMS SPECTRA AND LIMITS OF DETECTION

Standards with concentrations of 1 ng/ μ L and 100 pg/ μ L were prepared of TNT, RDX, PETN, NG, and NH_4NO_3 , and placed on the teflon membrane filter with a microliter syringe. The instrument conditions for our experiments are shown in Table 1.

The drift times, ion mobility (referenced to TNT, $K_0 = 1.451$) and the limit of detection for these 5 common explosive components are shown in Table 2. The detection limit for a given species was found to range from 200 pg to 80 ng.

Table 1. Operating Conditions for Explosives Detection.

Parameter	Setting
Drift Temperature	95 C
Inlet Temperature	215 C
Desorber Temperature	235 C
Desorption Time	4.3 s
Shutter Grid Pulse	200 μ s
Scan Cycle Time	24 ms
Drift Flow	350 ml/min
Sample Flow	300 ml/min
Exhaust Flow	650 ml/min

TABLE 2. Characteristic ions for some common explosives.

Peak	Proposed Species (-)	Mass	Drift Time(ms)	K_0 ($\text{cm}^2\text{V}^{-1}\text{S}^{-1}$)	L.O.D.
TNT	TNT-H	227	14.52	1.451	200 pg
RDX-1	RDX+Cl	257	15.19	1.387	200 pg
RDX-2	RDX+NO ₃	284	16.03	1.314	800 pg
RDX-3	RDX ₂ +Cl	479	22.22	0.948	1 ng
PETN-1	PETN-H	316	17.37	1.213	80 ng
PETN-2	PETN+Cl	351	18.40	1.145	200 pg
PETN-3	PETN+NO ₃	378	19.08	1.104	1 ng
NG-1	NG+Cl	262	15.73	1.339	50 pg
NG-2	NG+NO ₃	289	16.50	1.275	200 pg
NH ₄ NO ₃	H ₂ O+NO ₃	100	10.93	1.927	200 pg

It can be seen in Table 2 that more than one species is generated for some of the explosives. For example, three species labeled RDX-1, RDX-2 and RDX-3 are formed for RDX. It is theorized that these species are the chloride adduct (RDX+Cl)⁻, the nitrate adduct (RDX+NO₃)⁻, and an adduct between a neutral RDX molecule and the chloride adduct (RDX+(RDX+Cl))⁻. At 200 pg of RDX in the ionization region only the chloride adduct is formed but as the concentration increases to 1 ng more free neutral RDX molecules are present which can undergo ion molecule reactions with the chloride adduct. Proposed species for the other ions are presented as well. The plasmagram for RDX and PETN are shown in Figures 2 and 3, respectively. It should be pointed out that only the volatile ammonium nitrate is detected. Nitrates such as Na or K are not volatile at the desorption conditions used and are not detected and do not cause false alarms.

The exact nature of the species formed in the IMS under these conditions can only be decisively determined using an IMS/MS combination. A good deal of confidence can be

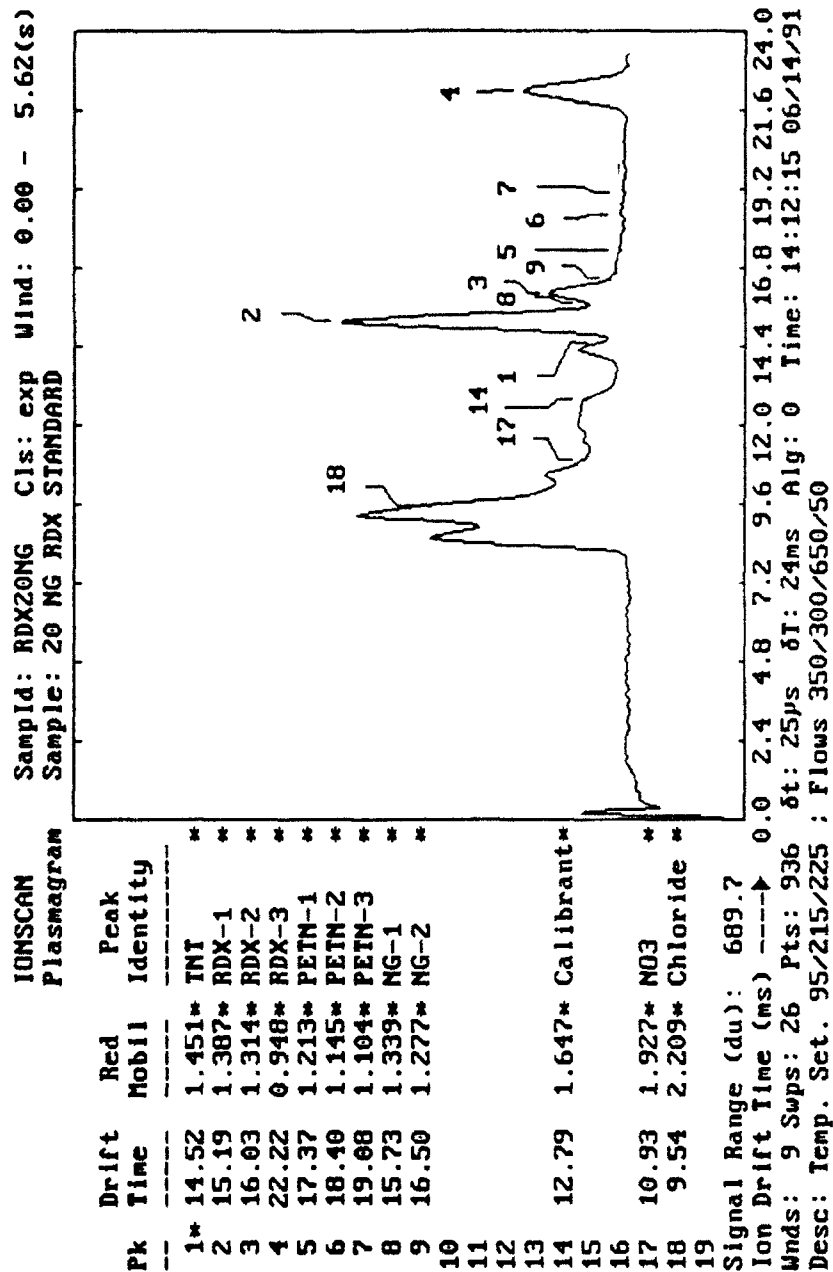


Figure 2. Plasmagram for 20 ng RDX standard. Plotted as intensity versus drift time. The table on the left shows those explosives programmed into the detector.

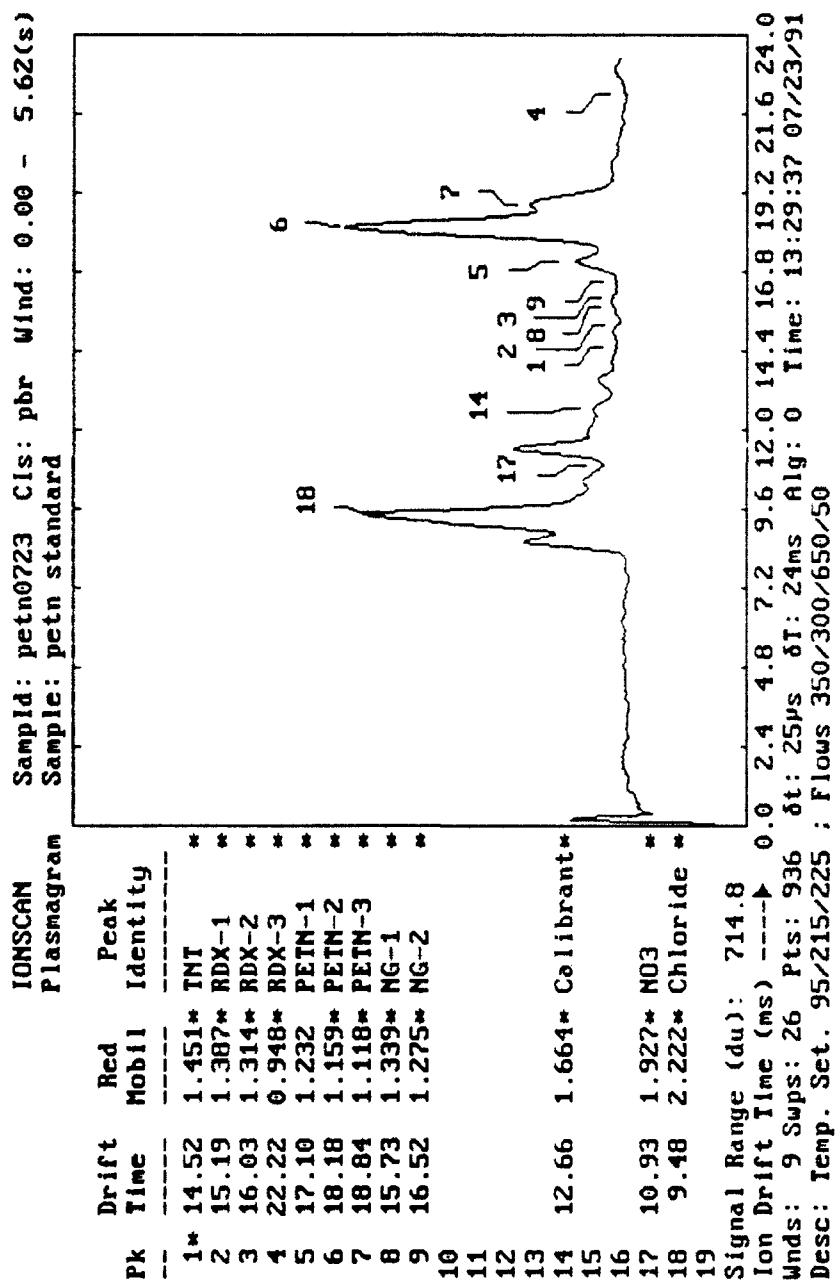


Figure 3. Plasmagram for 20ng of PETN standard.

gained in the assignment of the species by applying equations (2) and (4) to the data. As shown in Figure 4 an excellent agreement between the theoretical and observed behavior for the constant product of $(t \times K)$, drift time (t) vs mass, and a semilog plot of reduced mobility vs mass is observed as discussed in the theory section.

The formation of multiple species greatly increases the specificity and reduces the possibility of false alarm since the peak detection algorithms must recognize two of the three peaks for RDX, PETN and NG before the audible alarm will sound.

2.1 HAND AND SURFACE CONTAMINATION

Contamination of the hands has been shown to occur after handling commercial [11] and military explosives [12]. The persistence of these explosives on hands and evidence of contact transfer is well documented in forensic sciences [13,14]. IMS can be used to identify explosives on suspects or on their belongings. This evidence can provide probable cause for a search warrant, help identify a potential terrorist, and locate concealed explosives.

For this experiment a subject touched C-4 (RDX). The subject then enacted several normal stages in operating a car, including: opening and closing the hood, the driver side door, the trunk and handling the steering wheel, gearshift and keys. Samples were collected before and after the contact transfer from each of the touched areas of the car and from the subject's hands by vacuuming onto the teflon filter disk. An alternative sampling method which has also proven successful is to simply wipe the suspected surface with the sample collector. Careful procedures were followed to ensure that no cross contamination occurred by verifying that the sample disks and the IMS were clear of explosives before sample collection.

As shown in Table 3 the car surfaces and hands were negative for RDX prior to touching the explosive. After contact, all touched areas showed easily detectable RDX residue. In a separate experiment, after handling C-4, eight consecutive hand washings with soap and water were required before the IMS could no longer detect the RDX.

2.2 POST BLAST RESIDUE

Following a terrorist attack, rapid and accurate analysis of postblast residues plays a vital role in the bombing investigation. The first question often posed by an investigator following a blast is, "What was the explosive?" The analysis may provide the link between a suspect and the type of explosive used. Yelverton has demonstrated the detection of post-blast RDX vapor using a quartz tube pre-concentrator and IMS [15]. Because of its portability, the IMS can be taken to a bombing crime scene for preliminary analysis to aid law enforcement investigators.

We conducted a series of postblast residue experiments the results of which are summarized in Table 4. Samples were collected on the teflon membrane filters by vacuum, and the IMS was cleared between samples by running a blank.

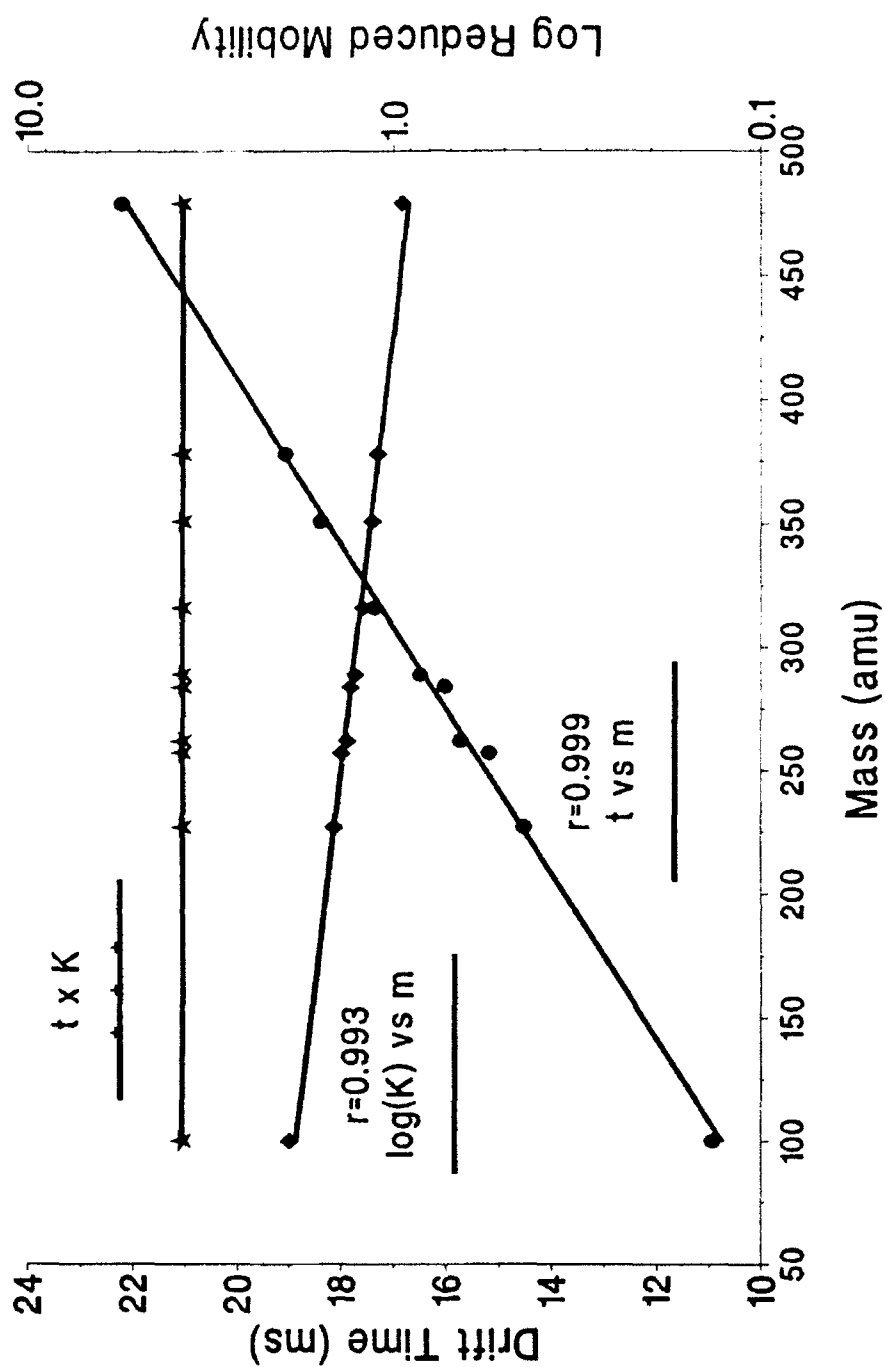


Figure 4. Characteristic ion behavior as a function of mass.

Table 3. Contact Transfer of C-4 from Hands to Automobile Surfaces

Car Area	Before Transfer	After Transfer
Hands	-	+
Hood	-	+
Door Handle	-	+
Hatch Back	-	+
Steering Wheel	-	+
Gear Shift	-	+
Keys	-	+

A number of improvised explosive devices (pipe bombs), were prepared. The pipes contained Hercules Green Dot, Scott Royal, Hercules Red Dot and Winchester Ball double-based smokeless powder, Pyrodex (a black powder substitute), and black powder. Following detonation, fragments of the pipes were recovered for analysis. A single fragment, just a few square inches in size was vacuumed. Fragments from the 4 pipes containing the double based smokeless powder alarmed positive for nitroglycerine. Figure 5 shows the NG plasmagram from a segment of the pipe which contained Green Dot double-based smokeless powder.

It can be seen that a third peak labeled with a drift time of 14.52 ms is also observed. This peak was determined to be dinitroglycerine, a reaction byproduct from the degradation of the NG, by analyzing standards of dinitroglycerine. It is only observed under conditions in which high concentrations of NG are present. Residue from the NG could still be detected 9 months later by reanalyzing the fragments. As shown in Table 4 the fragments of pipe from the pyrodex and black powder devices were negative for nitroglycerine and any other explosive.

One demolition block (1.25 lbs) of C-4 was placed in a suitcase containing 10 clothing items. Before the blast, the clothing and suitcase were clear of explosives. The C-4 was detonated and the post blast debris was collected. Postblast RDX residue was detected on all articles of clothing using the vacuum sample method. Figure 6 shows the plasmagram for the detection of RDX on pieces of a pair of blue jeans. RDX was also detected on pieces of cardboard liner and metal trim from the suitcase.

The terrorist access and use of SEMTEX is a major concern to law enforcement officials. A portable cassette/radio containing a small amount of SEMTEX was detonated. The remaining fragments and components were collected following the blast. Figure 7 shows the postblast RDX and PETN residue on a speaker magnet. It is of interest to note that only RDX and not both RDX and PETN were detected on a piece of plastic and the metal nameplate.

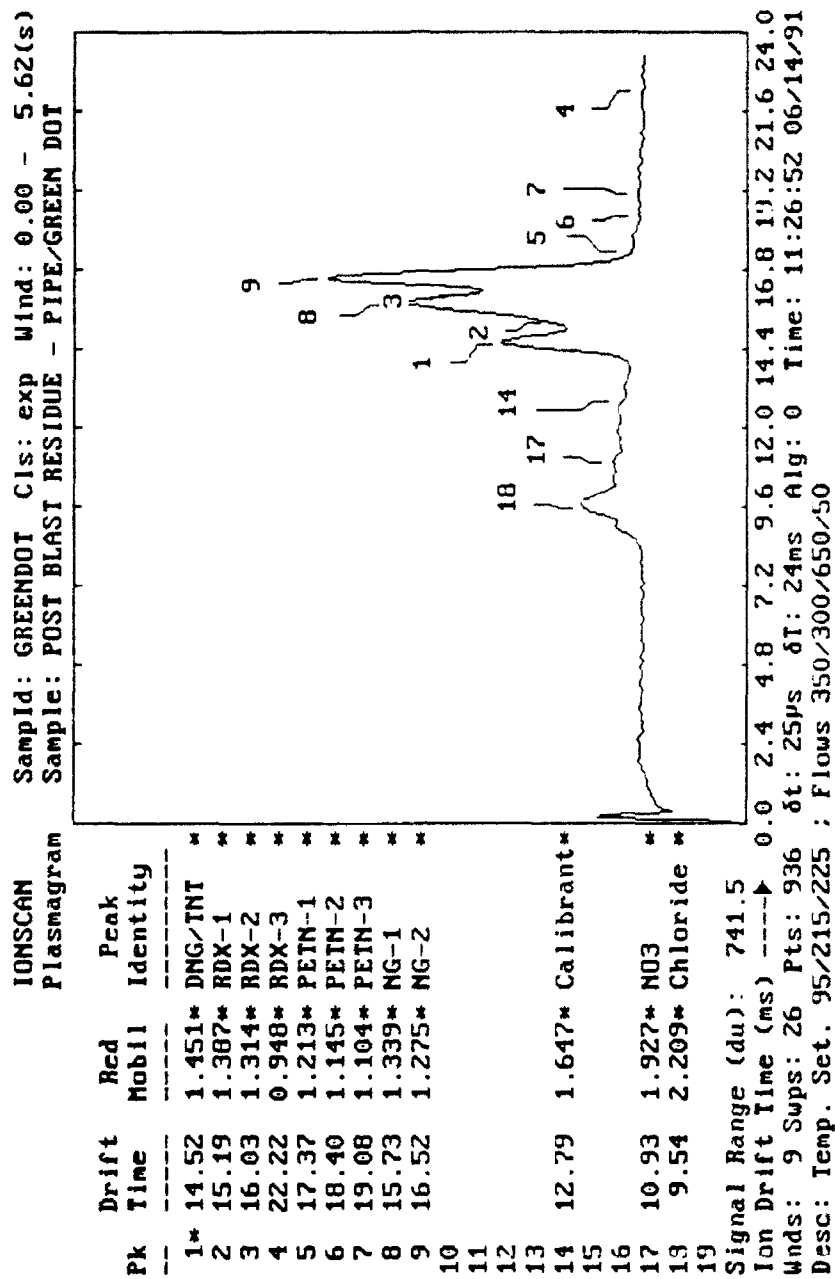


Figure 5. Detection of postblast NG residue on a pipe fragment.

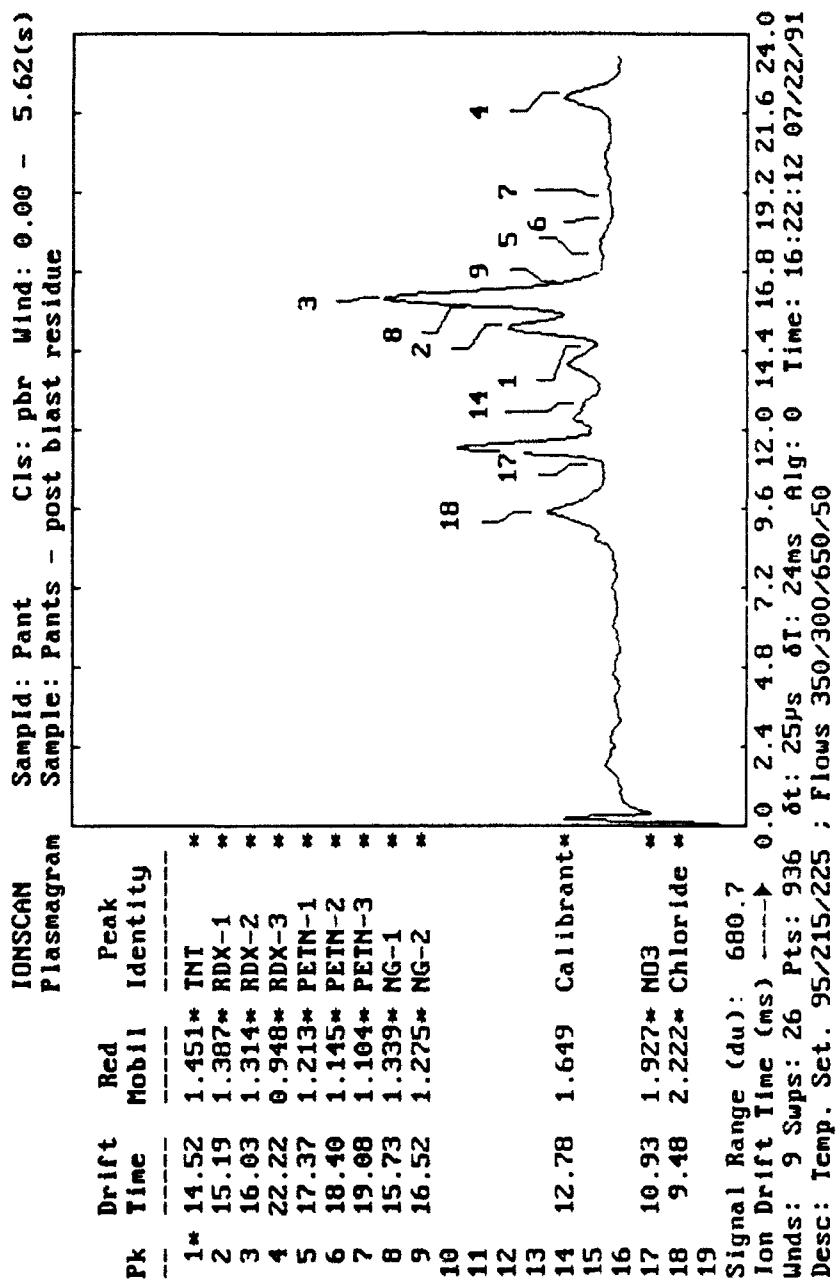


Figure 6. Detection of postblast RDX residue on a pair of pants.

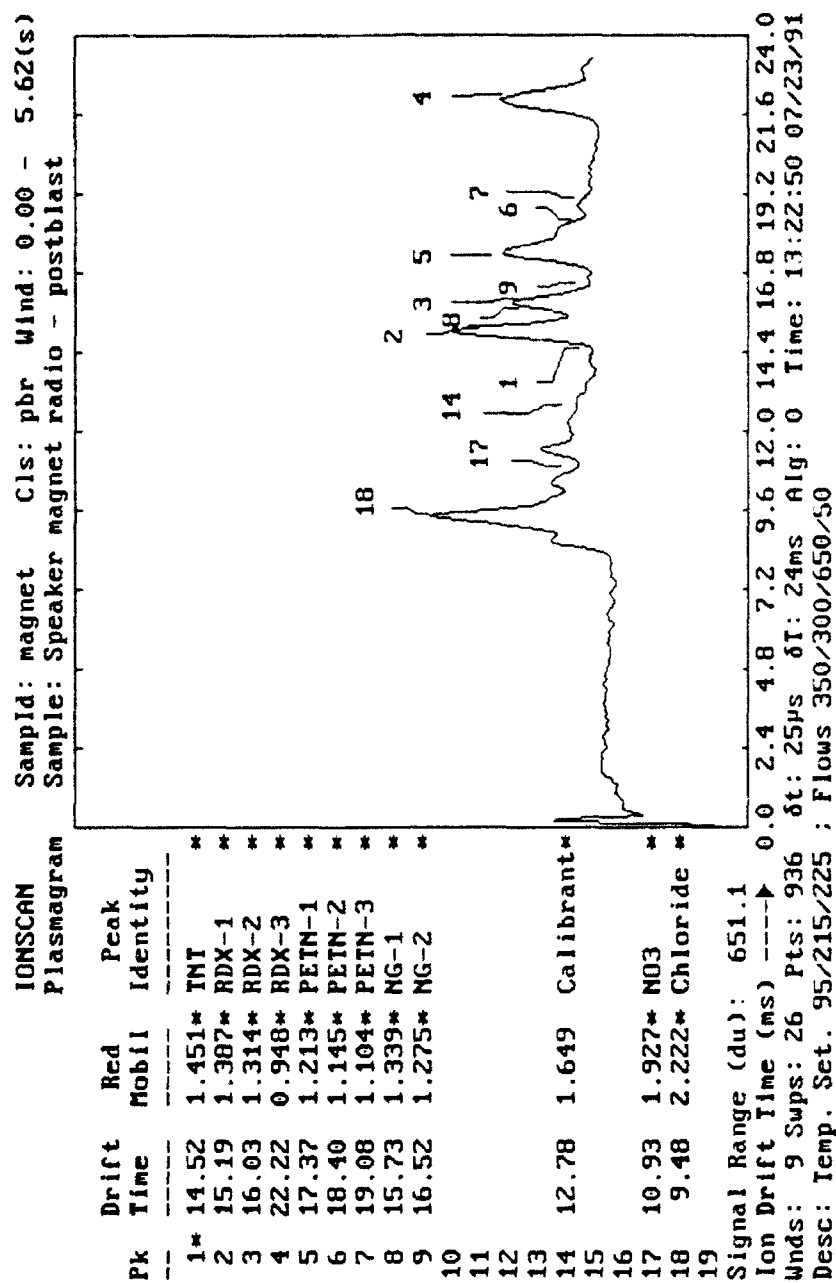


Figure 7. Detection of postblast PETN and RDX residue on a speaker magnet.

TABLE 4. Postblast Residue Analysis Results

Item and Explosive	Explosive Detected
<u>PIPE BOMBS</u>	
Green Dot	NG
Scott Royal	NG
Red Dot	NG
Winchester Ball	NG
Pyrodex	-
Black Powder	-
<u>SUITCASE (C-4)</u>	
10 items of clothing	RDX
Cardboard liner	RDX
Metal Rim	RDX
<u>Cassette/Radio (SEMTEX)</u>	
Speaker Magnet	RDX&PETN
Plastic Piece	RDX
Metal Nameplate	RDX

3. Conclusion

Ion mobility spectrometry offers forensic scientists, law enforcement investigators, and security personnel a new tool in trace explosives detection. Laboratory measurements of the sensitivity and specificity of the IMS showed detection as low as 200 pg for common explosives. In addition, results of experiments involving the detection of trace physical evidence from explosives in practical law enforcement scenarios have been presented.

The demonstrated retention of explosives on hands and the contact transfer to other surfaces provides the law enforcement investigator potential new sources for the collection of trace physical evidence when dealing with suspected terrorists or bombers. The detection of postblast residue from improvised explosive devices can aid the investigator at a bombing crime scene by providing a rapid means of screening evidence for further laboratory evaluation.

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EXPLOSIVE ANALYSIS BY CAPILLARY ELECTROPHORESIS

BRUCE R. McCORD and KELLY A. HARGADON,
*FBI Laboratory,
Forensic Science Research Unit,
Quantico, VA 22135, USA*

ABSTRACT. Capillary zone electrophoresis is a new analytical technique that can be used in the forensic analysis of anions resulting from post blast residues of explosives. Analyses previously carried out using ion chromatographic methods are easily converted to this new system, and the separations produced can be used as an independent confirmation of peak identity. The technique uses inverse photometric detection with a dichromate/borate buffer system and a DETA electroosmotic flow modifier. Aqueous extracts of residue are collected, extracted, and analyzed for characteristic ions resulting from the blast. The anions detected yield important clues in solving the problem of determining the type of explosive mixture used and its possible origin. The advantages of using capillary electrophoresis for residue analysis are discussed, and results of the analysis of various types of post blast residues are shown.

1. Introduction

The residue left behind in a low explosive bombing can offer important clues in determining the type of material used. For many years, the most powerful tool in these investigations has been ion chromatography (IC) [1]. Parts per million levels of the anions are easily detected and quantitated using this technique. The presence of such anions, produced as a result of the explosive reaction of oxidizer with fuel, is among the most important evidence used to determine the nature and source of the explosive.

Early instrumentation for IC consisted solely of suppressed conductivity chromatographic methods [2]. These procedures used a strong ion exchanger followed by a second column or membrane which neutralized the ionic eluent allowing only the conductivity of the sample ions to be detected. However, there were problems with these methods due to the wide variety of charge densities present in the ions found in explosive residues [3]. As a result, no single combination of column and eluent could achieve separation of all relevant ions. In addition, the eluent used for the separation of anionic species was bicarbonate, making detection of this particular ion impossible. To help alleviate these problems, gradient techniques and electronically compensated detectors were designed [4,5]. Another solution was the use of inverse photometric detection, a technique in which an absorbent eluent is used [6,7]. The advantage of these

non traditional IC techniques is that low capacity ion exchange resins can be used, allowing a wider range of sample ions to be analyzed on the same column [8,9].

Unfortunately, these improved IC methods still have problems with late eluting peaks and band broadening, reducing the sensitivity for ions such as perchlorate, carbonate and thiocyanate. In addition, the need to confirm peak identities necessitates a second chromatographic procedure.

The development of capillary electrophoresis (CE) for anion analysis has provided an opportunity to alleviate these problems [10,11]. This technique produces sharp peaks by achieving efficiencies of 70,000 or greater theoretical plates as opposed to about 3,000 theoretical plates for an IC system. Late eluting ions on the IC system such as perchlorate and thiocyanate occur much earlier in the CE system, improving analysis speed and detection limits. While still providing information in a format similar to IC, the CE system produces an orthogonal separation that is an ideal complement to IC and an excellent way to confirm peak identities [12].

2. Experimental Section

2.1 CAPILLARY ELECTROPHORESIS

The capillary electrophoresis system used was a Spectra Physics 1000 CE (San Jose, CA) equipped with a 75 μm ID fused silica column and a scanning ultraviolet detector. The detector was positioned at the positive end of the capillary (reversed polarity), and was operated in the dual wavelength UV mode at wavelengths of 280 nm and 205 nm. The operating voltage was -20,000 volts. Potassium dichromate, sodium tetraborate, boric acid, diethylenetriamine (DETA), and sodium hydroxide were used as received. The buffer system was prepared by adding 0.53 g of potassium dichromate, 0.76 g of sodium tetraborate, and 2.47 g of boric acid to 1 liter of deionized water [13]. The pH was adjusted to 7.65 with DETA, and the solution was filtered through a 0.45 μm nylon 66 filter. The resultant buffer solution was 2 mM in borate, 40 mM in boric acid, and 1.8 mM in dichromate. The 75 μm fused silica column was prepared for use by flushing for 2 minutes with 100 mM NaOH. Sample injection was performed using a hydrodynamic injection for 5 seconds.

2.2 ION CHROMATOGRAPHY

The ion chromatograph used for anion analysis was a Waters (Milford, MA) 600E Multisolvent Delivery System attached to a Kratos Spectra flow 783 variable UV detector set at 280 nm and a Waters WISP 710B autosampler. The column used was a Vydac 302IC4.6 (Hesperia, CA) with a flow rate of 2.5 ml/min and an injection volume of 25 μ l [9]. Detector signals were analyzed using a Waters 840 data system. Isophthalic acid (Aldrich) was used as received. To prepare the eluent, 0.75 g of the isophthalic acid was added to 3 liters of boiling water along with approximately 2 ml of 2 N KOH. Following dissolution of the acid, the solution was cooled and the pH adjusted to 4.6 using additional 2 N KOH.

2.3 SAMPLE PREPARATION

All solutions, standards, and extracts were prepared using 18 megohm deionized water. Pipe bombs containing a variety of explosive materials were deflagrated by the FBI Explosives Unit. Special care was taken in the treatment of these pipes in order to avoid sources of contamination. The pipes were rinsed with distilled water, air-dried, and carefully filled with the explosive preparation. To aid in this operation pipe threads were coated with petroleum jelly, and plastic bags were used in the filling operation, keeping the powder from contacting any surface near where the end cap screws back on. The pipe bombs were next rolled up in approximately 3 meters of chain link fence and set off while supported in the air between two posts. The fragments caught in the wire mesh of the fencing were then collected and taken back to the laboratory for processing. The residue from the blast was collected by washing the fragments with deionized water and filtering through a prerinsed 0.2 μ m syringe filter. These solutions were then left to dry overnight on watch glasses, and the dried crystalline material was collected for storage and later analysis.

3. RESULTS AND DISCUSSION

3.1 METHOD

Proper analysis of explosive residues requires reproducible retention times, minimal interferences, and the ability to clearly separate all relevant ions present in the blast residue. Among the most important of these ions are nitrite, nitrate, sulfate, chlorate, carbonate, and perchlorate. While it is not possible to determine the exact composition of the explosive following the blast of the

device, the presence or absence of these and other characteristic ions yield important clues in an investigation. By revealing the types and quantities of the ions produced, a good chromatographic method provides a "fingerprint" of the result of the blast.

CAPILLARY ELECTROPHORESIS SYSTEM

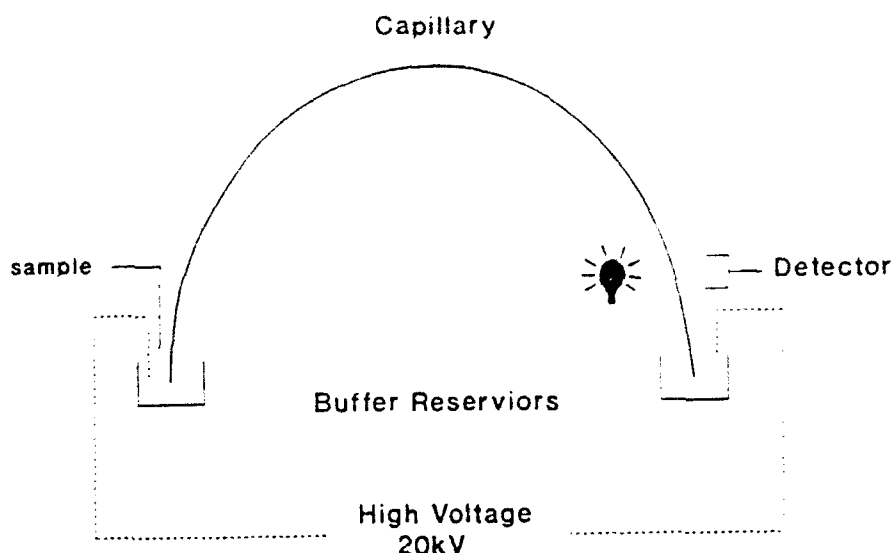


Figure 1. Capillary Electrophoresis System.

With these requirements in mind, we have investigated the CE separation. Capillary electrophoresis, Figure 1, functions by applying a potential difference of up to 20,000 kV across a thin fused silica capillary. Injection occurs by sipping a small amount of sample onto the column and then dipping the two ends of the column into a buffer solution and applying the voltage. Separation occurs due to the difference in charge to mass ratio of each solvated ion. The ions are swept past the detector by means of the induced or electroosmotic flow. For proper analysis this flow must be oriented in the direction of the positive electrode where the detector is located [14]. The electroosmotic flow modifier, DETA, coats the capillary with positively charged ions, orienting this osmotic flow towards the detector and allowing the anion separation to be performed quickly and efficiently. Since many anions do not absorb well in the ultraviolet,

detection occurs by monitoring the loss in absorbance of the dichromate eluent at 280 nm.

For the CE system, the minimum detectable concentration was 0.5 ppm, while that for the IC system was 2 ppm. It should also be noted that the sample injection volume used in the CE system was 1000 times less than that of the IC.

The dynamic range was 1 to 50 ppm. This can be compared to the 5 to 200 ppm range of concentrations applicable to our IC system. The practical result of these studies was that effective analysis of residue by both systems requires that the residue solution analyzed by the IC system had to be diluted 5 to 10 fold in order to achieve the most effective CE separation.

A useful technique for determining peak identity was to perform a second analysis with detection at a lower wavelength. At 205 nm, bromide, nitrite, nitrate, and thiocyanate produce peaks in a positive direction due to their UV absorbance. Anions that do not absorb at this wavelength continue to produce peaks in the negative direction. This yields an electropherogram that while less sensitive than that at 280 nm produces a distinctive pattern of positive and negative peaks. Figure 2 shows the results of an analysis of our standard recorded at 205 and 280 nm using a scanning UV detector (Spectra Physics 1000).

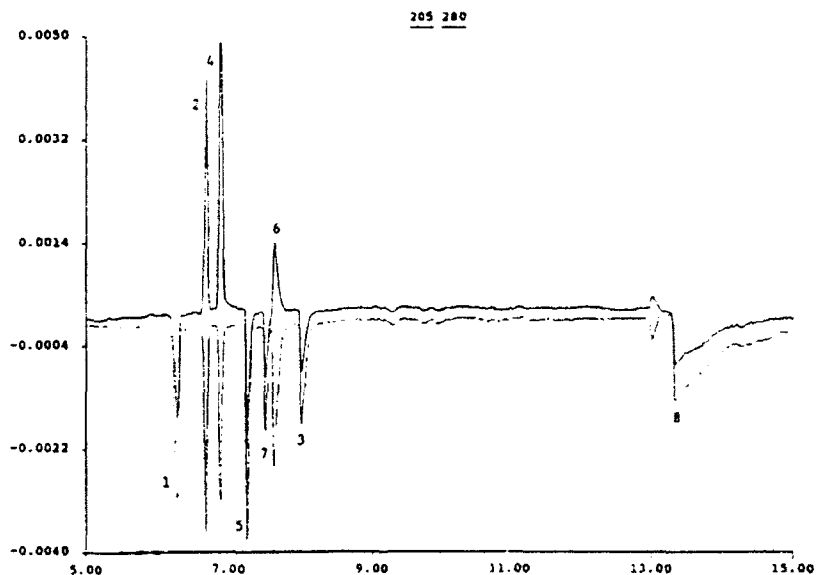


Figure 2. Anion Standard Containing Ions Present in Explosive Residue. Analysis performed at 205 and 280 nm using Capillary Electrophoresis. Peak identification: 1-Cl⁻, 2-NO₂⁻, 3-ClO₃⁻, 4-NO₃⁻, 5-SO₄²⁻, 6-SCN⁻, 7-ClO₄⁻, 8-HCO₃⁻.

One of the reasons CE is so valuable for peak confirmation of IC results is the due to the difference in separation mechanism. Capillary electrophoresis separations are based on differences in charge to mass ratios of the sample ions while IC separations are the result of complex interactions between the ions and the stationary phase. This can be seen clearly in Figure 3 which shows the nearly orthogonal relationship in the relative retention times of the two techniques [12].

Retention Time Relative to SO_4

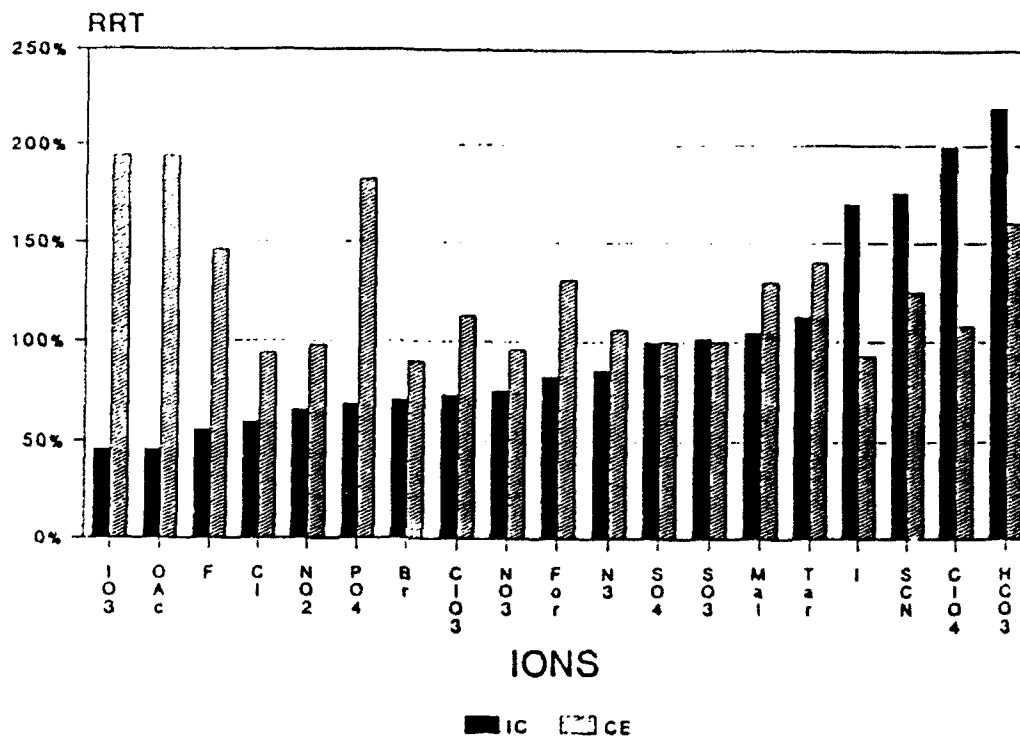


Figure 3. Comparison of Elution Order in Capillary Electrophoresis and Ion Chromatography.

These differences in elution order make peak interferences easy to detect as overlapping peaks in one technique are likely to be widely separated in the other. For example in IC, ions such as phosphate, bromide, and thiocyanate can cause interferences with the oxidizer ions nitrite, chlorate, and perchlorate respectively. In CE however, these ions are well separated from each other. Confirmation of identity can also be made by changing the wavelength in CE. In fact, CE has become the primary method of choice in our laboratory due to the many advantages inherent in the method, and we now use IC as a secondary confirmation technique allowing us to elucidate problematic CE results.

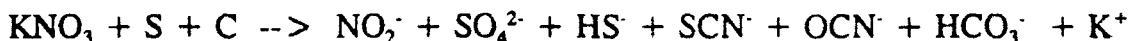
3.2 ANALYSIS OF PIPE BOMBS

To test the capabilities of the capillary electrophoresis system, a series of experiments were conducted by initiating pipe bombs containing various explosive mixtures and carrying the fragments back to the laboratory. The explosives were set off on an explosives ordnance demolition range and prepared in the manner described above. Extreme care was taken in the preparation and manipulation of the unexploded devices.

Analysis of the explosive residues was conducted in an effort to document the anionic chemical profile of the residue. The fragments of each pipe were also sampled in two different locations to check for variations in the amounts of ions present and to look for the presence of pockets of unexploded material.

One persistent problem for the forensic chemist in analyzing evidence from bomb residues is the lack of an extensive knowledge base on what may be present in the residue. Typically, the development of new analysis techniques proceeds piecemeal, with conclusions based on very small sets of data. This is because experiments of this nature can only be performed in isolated and remote locations, and because these devices are extremely dangerous. Thus knowledge of the chemical makeup of explosive residues often comes from actual criminal casework; data in which little is known of the conditions used in preparation of the device or in the collection of the evidence.

Figures 4 and 5 show the results from the IC and CE analyses of a pipe bomb filled with black powder. This explosive contains potassium nitrate, sulfur, and charcoal. The results show a wide variety of ions present in the anionic residue. These ions are the products and reactants of the following equation:



Note the difference in efficiency between the IC and CE analyses. The peak broadening that occurs with the late eluting ion SCN^- in the IC analysis limits sensitivity for this ion. In Figure 4, peak number 3, appears at the same position as chlorate in the standard. Chlorate, however, is not present in black powder. Further analysis by CE, Figure 5, reveals this peak to be cyanate. Thus without the use of CE the investigator would not be able to rule out the presence of chlorate in the original explosive mixture. This observation underscores the importance of the confirmation step in our analysis.

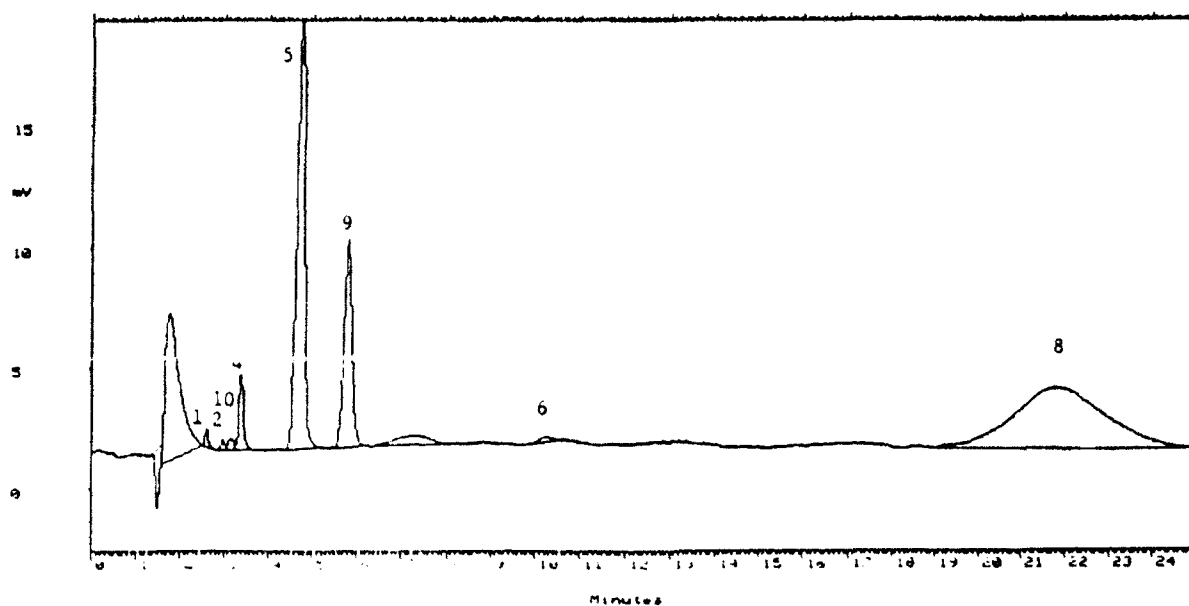


Figure 4. Ion Chromatogram of Black Powder Pipe Bomb Residue. Peak identification: 1- Cl^- , 2- NO_2^- , 4- NO_3^- , 5- SO_4^{2-} , 6- SCN^- , 8- HCO_3^- , 9- HS^- , 10- OCN^- .

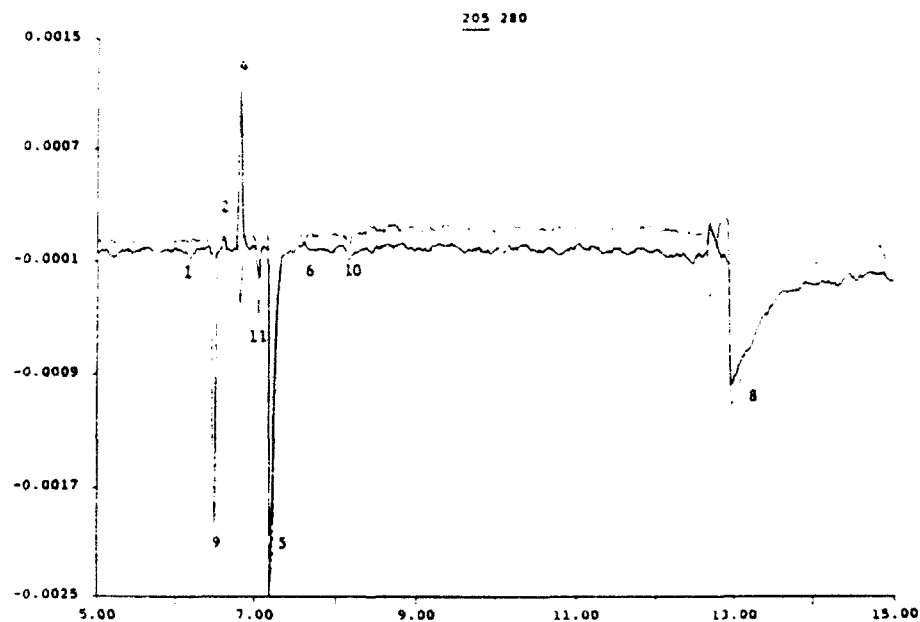


Figure 5. Electrophorogram of Black Powder Pipe Bomb Residue. Peak identification: 1- Cl^- , 2- NO_2^- , 4- NO_3^- , 5- SO_4^{2-} , 6- SCN^- , 8- HCO_3^- , 9- HS^- , 10- OCN^- , 11-unk.

Figures 6 and 7 show other examples of the application of capillary electrophoresis to bomb residue. Figure 6 shows the CE analysis of a pyrodex pipe bomb. The electropherogram illustrates the advantage of dual wavelength detection. Note peak number 9, sulfide. At 205 nm the sensitivity for this peak reaches a minimum due to a certain amount of inherent absorbtivity. Thus only a peak at 280 nm appears. Nitrite, nitrate, and thiocyanate also appear as positive peaks in this analysis. The ability to overlay the analysis of at wavelengths gives a great deal of confidence in assignment of peaks.

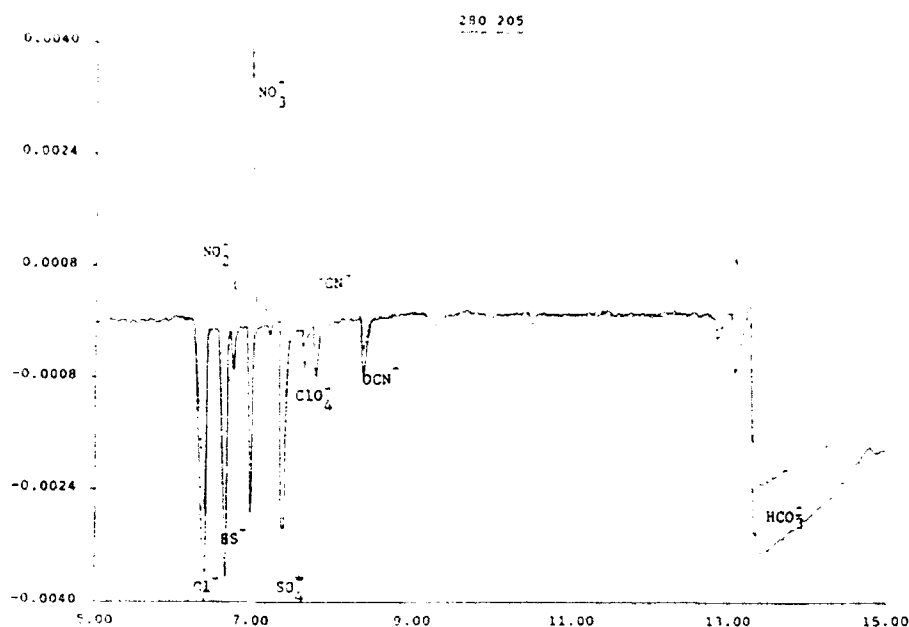


Figure 6. Electropherogram of Pyrodex Pipe Bomb Residue.

Figure 7 shows the analysis of the residue of a flash powder obtained from a firecracker. This flash powder probably contained mixture of sulfur, aluminum, and potassium perchlorate. The small nitrate peak in this sample is the likely result of a black powder fuse. The perchlorate peak is sharp and well defined. Note the absence of any chlorate ion. This ion has been sometimes proposed as an intermediate present in residue resulting from perchlorate oxidizers. [3,9] It is not present in this sample or in the the pyrodex residue and speculation about its existence may have been the result of an interfering peak such as cyanate.

Among the threads and end caps of the pipe bombs, relatively more of the explosive mixture was left unburned, while fragments from the pipe center had correspondingly less unburned material. Figure 8 shows the overlay of an

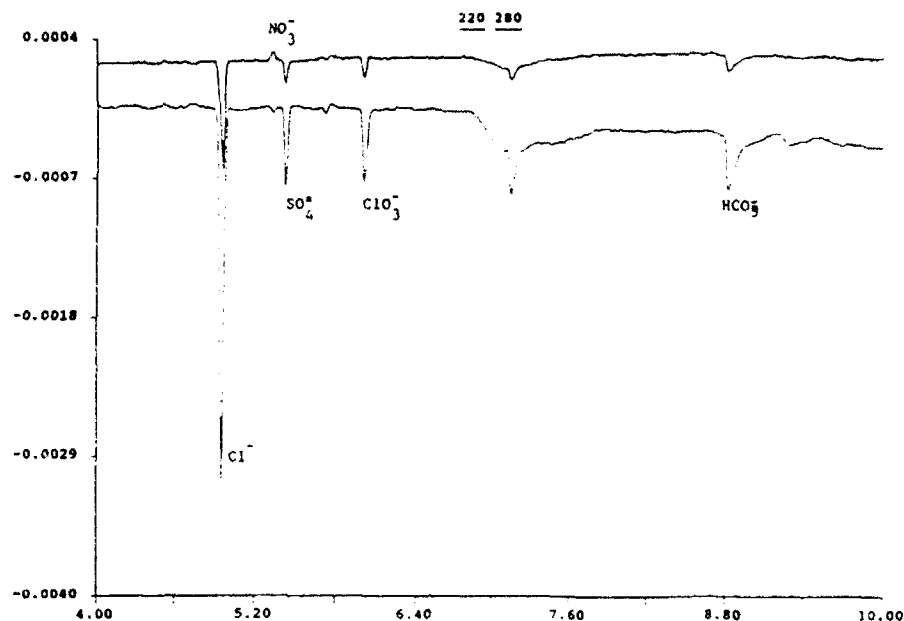


Figure 7. Electropherogram of Flash Powder Residue.

analysis of two different sections of a black powder pipe bomb. The sample obtained from the pipe threads contained relatively more nitrate and sulfate while the sample from the center of the pipe contained more of the other reaction products. This finding underscores the importance of examining all pieces of evidence, particularly in situations where only small amounts of residue remain.

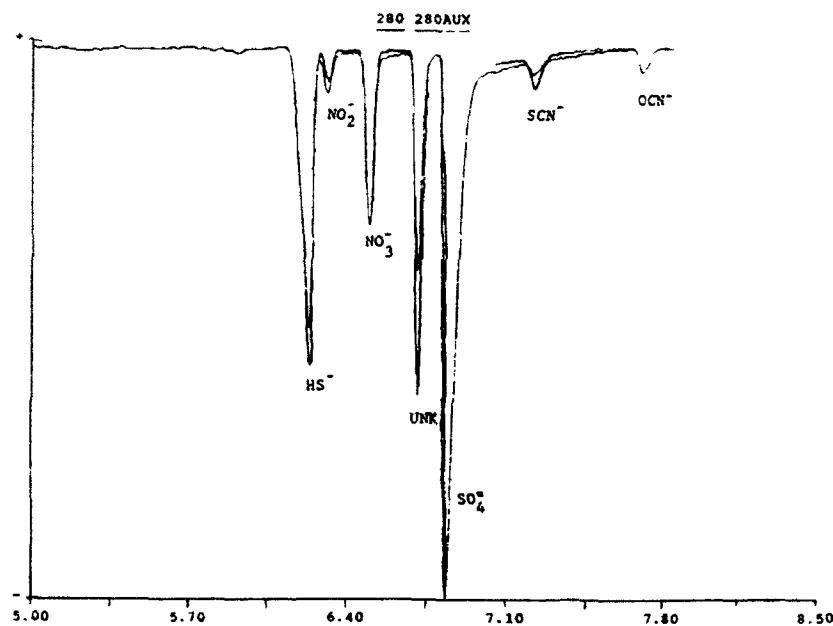


Figure 8. Electropherogram of Blackpowder Pipe Bomb Residue Sampled at Pipe Center and Threads. 280Aux trace is from the pipe center.

4. Conclusions

The large differences in separation mode and action of the two techniques give great assistance to the analyst in determining the nature of the sample. Use of IC and CE in tandem greatly reduces problems caused by interfering ions and allows easy peak confirmation. In addition, the inherent sensitivity advantage of CE works in concert with the greater capacity of the IC system allowing a wide variety of concentrations and types of residue to be screened. For these reasons, we have found that the application of these two techniques greatly expands the capability of our laboratory in undertaking explosive residue analyses.

5. Acknowledgements

We would like to thank Frederick Whitehurst, Amy Sirignano, and Steve Burmeister for their support and technical assistance, and the Explosives Unit of the FBI Laboratory for their help in the preparation and initiation of the pipe bombs.

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THE ANALYSIS OF THE EXPLOSIVES OF THE PAPER DETONATOR

T. Z. Hong, C. P. Tang & K. Lin
Dept. of Chemistry, Chung-Shan Institute of
Science & Technology
P.O. BOX 90008-17 Lung-Tan
Taiwan, Rep. of China

ABSTRACT. A number of paper detonators were found in a smuggling case. The explosives were coated on brown paper and wrapped as cylinder tubes. It could easily pass X-ray examination during a security check. Two different colored explosive ingredients were isolated from the detonator. A locally developed explosive test kit based on spot-test theory as well as IR and GC/MS spectrometric methods were used to identify the explosive compounds. The orange colored ingredients were identified to be RDX with a small amount of wax and orange color pigments. The brown colored sample was identified to be diazodinitrophenol (DDNP) primer. The paper was coated with wax in order to prevent moisture penetration. This detonator, which is activated by a fuse cord (black powder), has the capability to initiate a TNT charge.

INTRODUCTION

Recently, a typical paper detonator was discovered by the coastguard authority in Taiwan. This detonator could be exploded with a safety fuse cord (black powder). It has the capability to initiate a TNT charge. The weight of each cylindrical paper detonator is 2.64 gram. Its o.d is 8 mm and length 45.7mm (Figure 1). Two different color explosive samples were wrapped in the kraft paper (0.86 mm. thickness). The lower part has an orange color, and the upper part a brown color.

Usually, initial detonating agents are lead azide $[Pb(N_3)_2]$, mercury

fulminate $[Hg(ONC)_2]$, lead styphnate $[C_{12}H_6N_6O_6Pb]$, Diazodinitrophenol (DDNP) O=[N+]([O-])c1cc([N+](=O)[O-])ccc1[N+](=O)[O-], Tetracene C1=CC=CC=C2C(=C1)N=CN=C(N2)C(=O)N=NNH-C(=O)NH2.

The paper detonator is assumed to contain one of these compounds. Various analytical tools were applied in its analysis.

APPARATUS

- (1). Explosive test kits -- include six test sets. The reagents sealed in glass ampules packed in PE bags. The test kits are used to detect the black powder (potassium nitrate \ sulphur \ carbon) \ homemade black powder (potassium chlorate \ sulphur \ carbon) \ DNT \ TNT \ Picric acid \ Tetryl \ RDX \ HMX \ Pb(SCN)₂ and Nitroesters (such as NG \ NC \ PETN)
- (2). X-Ray Spectrometer, PHILIPS PW1410.
- (3). FTIR, Nicolet 170 sx.
- (4). Mass Spectrometer, Finnigan 4023.
- (5). High Performance Liquid Chromatograph, Waters.441.

METHODS

The explosive samples inside the paper detonator were analyzed separately in three parts according to its colors and coating material. The procedures were:

- (1). Screen test:use the explosive test kit to make a screen test of the unknown explosives. The sample identification bags contain one to three glass ampules with reagents sealed in the ampules. While identifying the explosives, put a small amount of sample into the P.E. bag and break the ampules one after another starting from the left side. The characteristic color will appear if the compound consists the corresponding functional group.
- (2). Metal elements: detect the metal elements by X-ray (fluorescence) spectrometry.
- (3). IR spectrometry:use IR spectrometry to identify compounds by "fingerprint"comparison and the location of functional groups in unknown compounds.
- (4). Mass spectrometry:determine the molecular weight of unknown samples.
- (5). Solvent extraction:the coating material of kraft paper was extracted with petroleum ether.

RESULTS AND DISCUSSION

- (1). The analysis of orange colored sample

The orange colored sample was analyzed by the Explosive test kits. Its reaction with the reagents of test set 1 (diphenylamine in conc. H₂SO₄/H₂O) showed a blue color [1] . It may contain a functional group such as -ONO₂, -NNO₂ or ClO₃⁻ etc. While reacting with the reagents of test set 5 (H₂SO₄/chromotropic acid disodium salt/H₂O), it gave red purple color products. The results indicate that this unknown compound may contain RDX or HMX.

As analyzed by X-ray (fluorescence) spectrometry, no metal element was detected.

Its IR spectrum (Fig.2) shows the major peaks at 3074 cm⁻¹, 3065cm⁻¹ (CH stretching mode of nitramine), 2918cm⁻¹, 2849cm⁻¹, 1593cm⁻¹, 1573cm⁻¹, 1532cm⁻¹, 1311cm⁻¹ and 1267cm⁻¹. Comparing with the standard spectrum of RDX (Fig.3), they are similar except for two additional peaks (2918cm⁻¹, 2849cm⁻¹), which may be from the CH stretching of hydrocarbon such as wax contained in the sample. Explosives such as composition A-3(RDX 91% , wax9%) and composition A-4 (RDX 97%, wax 3%), both contain RDX and wax. Comparision of the IR spectrum of the sample with composition A-4 (Fig.4) and composition A-3 (Fig.5), showed a good a match with compos-



Fig 1. The photograph of paper detonator.

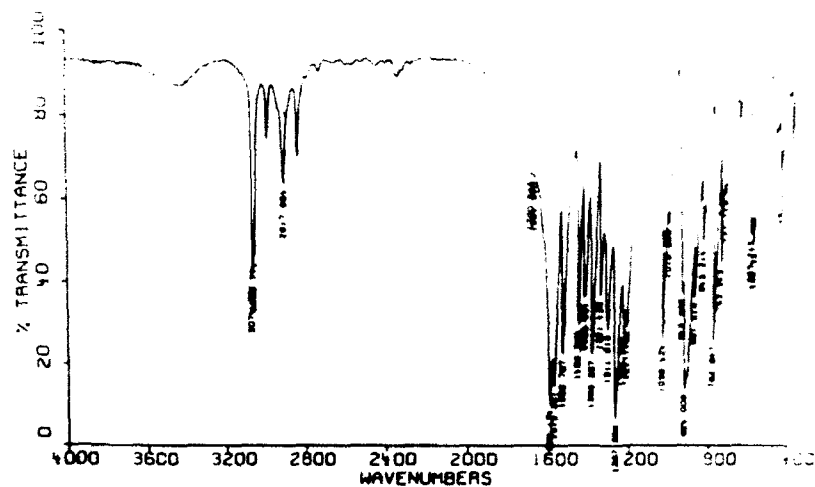


Fig 2. The IR spectrum of orange colored sample.

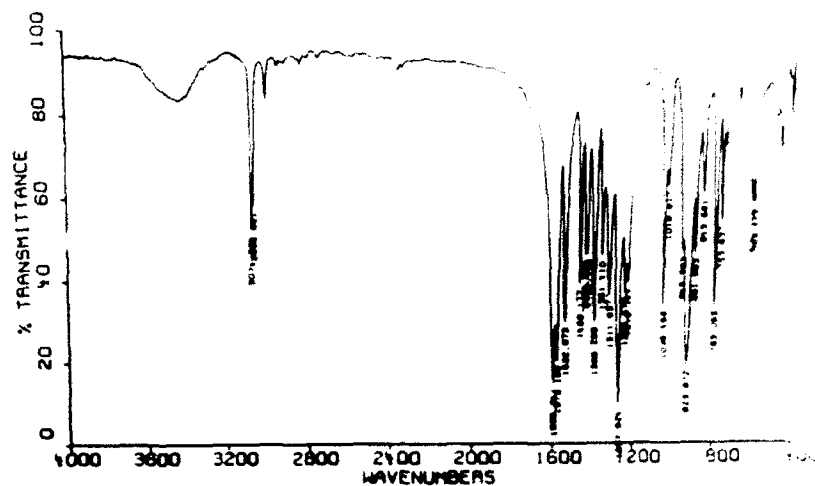


Fig 3. The IR spectrum of RDX.

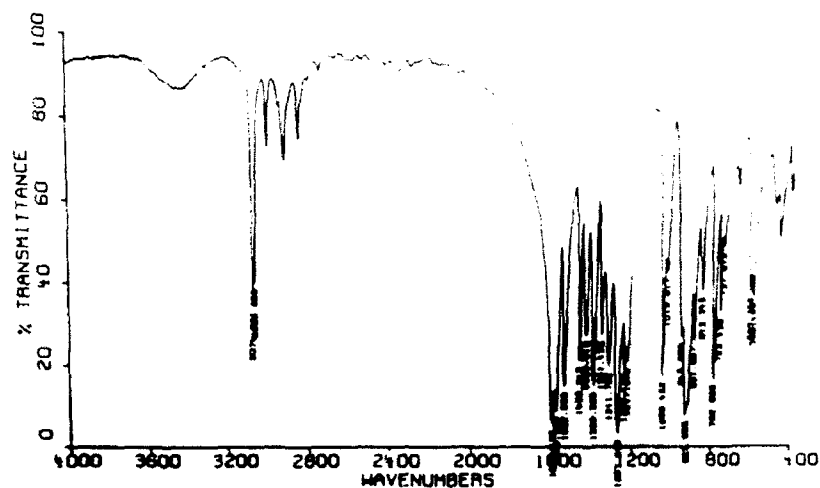


Fig 4. The IR spectrum of Composition A-4

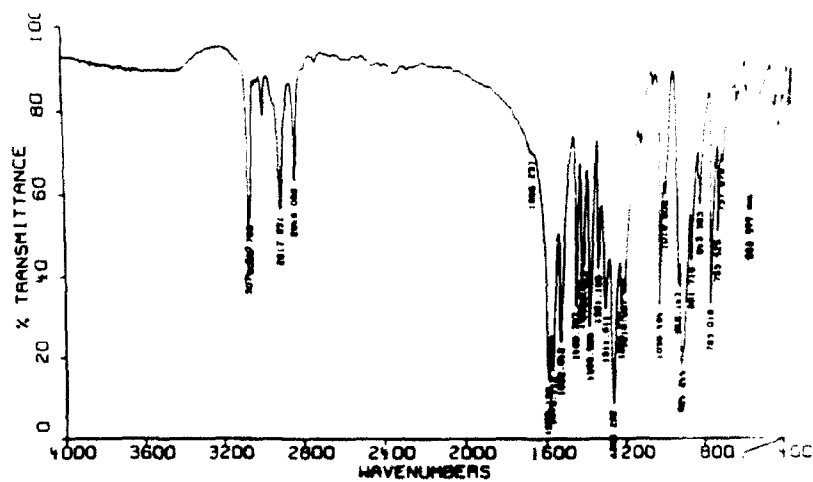


Fig 5. The IR spectrum of Composition A-3

ition A-4.

HPLC was used for quantitative analysis in order to determine the RDX content.

HPLC condition:

column: C-18

eluent: CH₃OH/H₂O (1:1)

flow rate: 1 cc/min

detector: UV detector (254nm)

The quantities of RDX and wax with orange color pigments are shown in table 1.

Table 1. quantitative results of orange colored Compound

Ingredient	Percentage %
RDX	94.1±1.0
Wax + other compounds	5.9±1.0

(2). The analysis of brown colored sample

The brown colored sample was analyzed by the Explosive test kits. Its reaction with the reagents of test set 2(1%(W/V)KOH in acetone/ethanol, 1/4 solution[2]) presented a yellow to orange color. No special color reaction with the other five test set reagents. This indicates that the brown color compound may contain polynitroaromatic compounds. But it should not be TNT, DNT or Tetryl [3].

As analyzed by X-ray (fluorescence) spectrometry, no metal element was detected in this sample.

Its IR spectrum (Fig.6) shows peaks at 3079cm⁻¹ and 905cm⁻¹, 710cm⁻¹. they are the CH stretching and bending of aromatic compounds respectively. Peaks at 1553cm⁻¹ and 1323cm⁻¹ should be the asymmetric and symmetric stretching mode of NO₂. The peaks at 2211 cm⁻¹ may be the -O-N=N- functional group of DDNP. Further identification by mass spectrometer was carried out.

Its ion peaks in the PCI-CH₄ mass spectrum (Fig.7) are m/z. 251 (M+C₃H₅)⁺, 211(M+H)⁺, 194(M-O)⁺, 183(M+H-N₂)⁺ and 166(M-2N-O)⁺. The NCI-CH₄ mass spectrum of this sample is shown in Fig 8 with ion peaks at m/z 318(M+2NO₂+O)⁺, 212(M+2H)⁺, 199(M-2N+OH)⁺, 182(M-2N)⁺, 167(M+H-2N-O)⁺ ect. The molecular ion is m/z 210.

From the analytical results of color reaction of explosive test kits, IR spectrum and mass spectra, the brown explosive sample was identified as diazodinitrophenol.

(3). Coating materials of kraft paper

IR spectrum in KBr cell of coating reagent of kraft paper is shown in Fig.9. In the IR spectrum absorptions at 2917cm⁻¹, 2849cm⁻¹, 1426cm⁻¹ are the CH stretching and bending of alkane. It matches quite well with the IR spectrum of wax (Fig.10). The coating wax of the paper detonator is obvious to prevent moisture penetration.

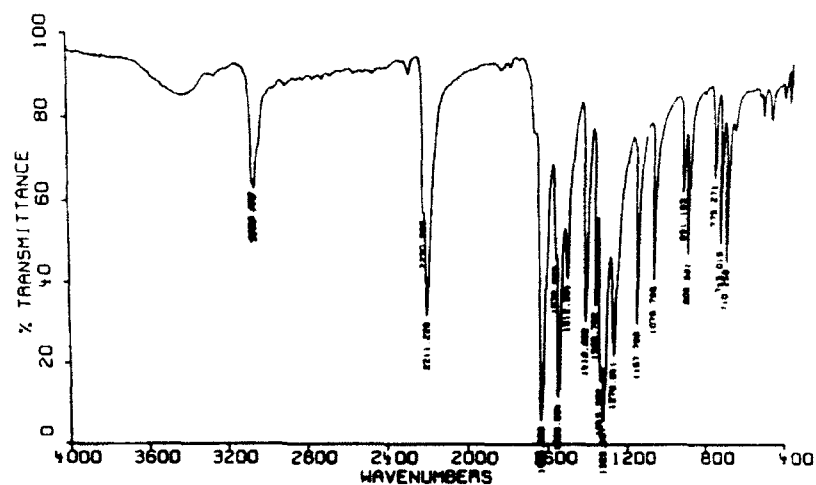
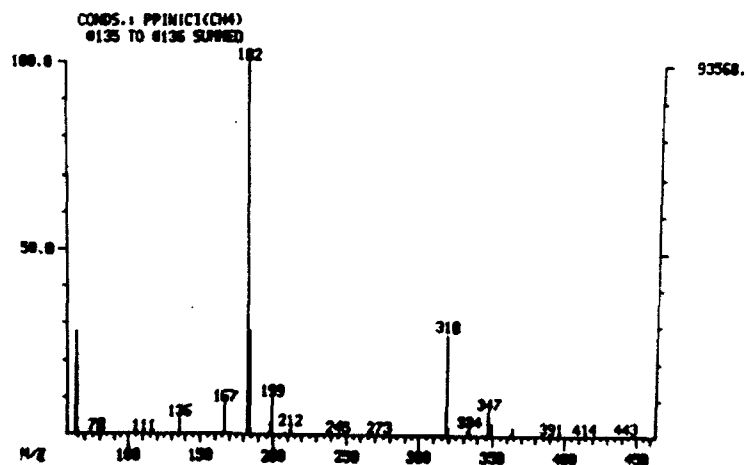


Fig 6. The IR spectrum of brown colored sample.

Fig 7. The PCI-CH₄ mass spectrum of brown colored sample.Fig 8. The NCI-CH₄ mass spectrum of brown colored sample.

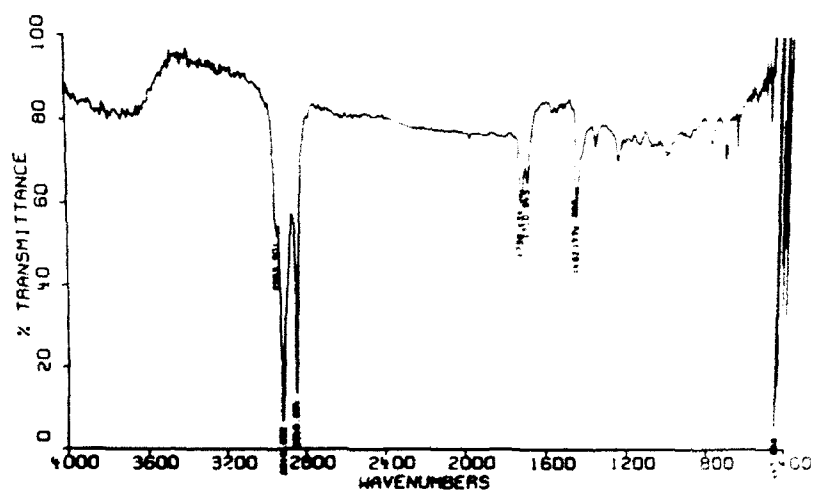


Fig 9. The IR spectrum of coating material of kraft paper.

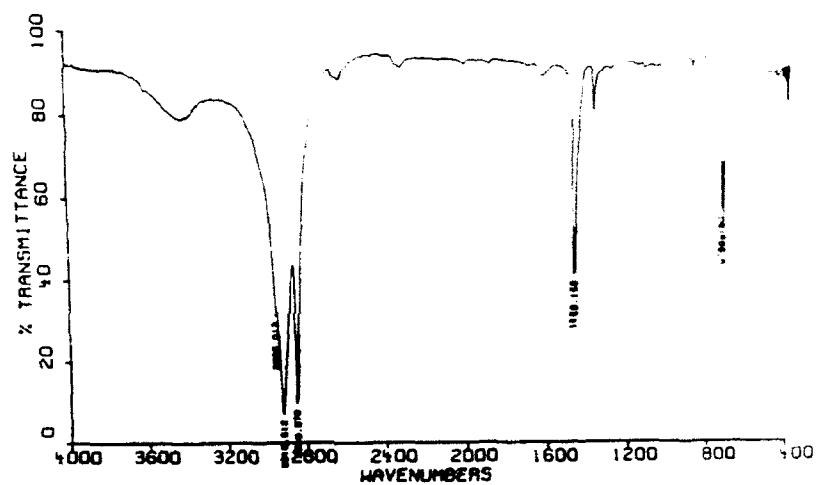


Fig 10. The IR spectrum of wax.

CONCLUSION

From spot-test kits, IR and mass spectrometric analysis results, we found that the ingredients of the paper detonator are composition A-4 and DDNP primer. Because the composition A-4 contained desensitizer wax, the more powerful initiating agent DDNP is suitable to initiate it. These paper detonators can be initiated when connected with a safety fuse cord. No other auxiliary devices such as electrical cell, wire or initiator are needed. It is an easy method to initiate an explosion.

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GAS CHROMATOGRAPHIC RETENTION INDICES OF EXPLOSIVES AND NITRO-COMPOUNDS

JOHN R. HOBBS and EDWARD P. CONDE
Volpe National Transportation Systems Center
Research and Special Programs Administration
U. S. Department of Transportation
Kendall Square
Cambridge, MA 02142, USA

ABSTRACT. Both, isothermal (Kovats) and linear temperature programmed retention indices, were determined for nitro-alkanes, nitro-aromatics, and explosives on a J&W 0.2 mm diameter, 30 meter DB-5 column with a 0.25 micron film thickness. A Hewlett Packard Model 5890 gas chromatograph, equipped with a split/splitless injector at 145 ° C and a Model 5970 mass spectrometer or a flame ionization detector were used to obtain the data. The gas chromatograph was operated isothermal at 140 ° C or linear-temperature programmed from 40 ° C to 300 ° C at a rate of 5 ° C per minute. Within a homologous series, the linear-temperature programmed retention indices are a linear function of the boiling point. In general, the linear-temperature programmed retention indices are a linear function of the retention time. These data are being used to form a retention-index data base for the identification of explosives compounds by gas chromatography.

1. Introduction

The vapor detection of concealed explosives requires identification of their characteristic vapors. Capillary gas chromatography is often used to separate and analyze trace vapors in the headspace of explosives; but qualitative analysis is often difficult because standards for retention time comparison are not available for the explosives and other trace impurities. The adjusted retention time is characteristic of a given peak determined for a specific column size, stationary phase and loading, carrier gas flow rate, column temperature, and other factors. Since the adjusted retention time depends on several variables, it is difficult to reproduce from day to day in the same laboratory with the same equipment, and nearly impossible to

from laboratory to laboratory. To aid in the identification of explosives and their impurities, retention indices would be most helpful. The retention index system developed by Kovats [1,2] provides a method of reporting relative retention that can be compared from laboratory to laboratory and from column to column, because it uses a single set of reference compounds for all samples and utilizes ratios of retention times, rather than the times themselves. A search of the literature revealed that retention indices have not been published for most explosives and nitro- compounds.

1.1 ISOTHERMAL (KOVATS) RETENTION INDICES

Kovats choose as the set of reference materials the normal (straight chain) saturated hydrocarbons, since they are cheap, readily available, stable, and chromatograph well on all stationary phases. When a homologous series of compounds is analyzed isothermally, the logarithms of the adjusted retention times of the peaks are linearly related to the number of carbon atoms of the compound. The retention index for any of the normal hydrocarbons is defined to be 100 times its carbon number. All other compounds are treated as if they were normal hydrocarbons with fractional carbon numbers. The retention index, RI, is a number relating the adjusted retention time of a compound X to the adjusted retention times of normal hydrocarbons.

The adjusted retention time, t'_r , is defined as

$$t'_r = t_r - t_m \quad (1)$$

where t'_r = adjusted retention time;

t_r = measured retention time;

t_m = retention time of unretained peak.

The Isothermal Retention Index, RI_x is given by:

$$RI_x = RI_b + \frac{\log t'_{rx} - \log t'_{rb}}{\log t'_{ra} - \log t'_{rb}} \times [RI_a - RI_b] \quad (2)$$

where RI_x = Retention Index of unknown peak x;

RI_b = Isothermal Retention Index of the nearest reference peak before peak x;

RI_a = Isothermal Retention Index of the nearest reference peak after peak x;

t'_{rx} = adjusted retention time of peak x;

t'_{rb} = adjusted retention time of the nearest reference peak before peak x;

t'_{ra} = adjusted retention time of the nearest reference peak after peak x.

1.2 LINEAR TEMPERATURE PROGRAMMED RETENTION INDICES

The Linear Programmed Retention Index is calculated by linear interpolation between two reference peaks with known indices [3]. In this calculation the dead time is zero and the Retention Index is calculated by:

$$RI_x = RI_b + \frac{t_{rx} - t_{rb}}{t_{ra} - t_{rb}} \times (RI_a - RI_b) \quad (3)$$

where RI_x = programmed Retention Index of peak x;

RI_b = programmed Retention Index of the nearest reference peak before peak x;

RI_a = programmed Retention Index of the nearest reference peak after peak x;

t_{rx} = absolute retention time of peak x;

t_{rb} = absolute retention time of the nearest reference peak before peak x;

t_{ra} = absolute retention time of the nearest reference peak after peak x.

2. Experimental

2.1 EXPLOSIVES SAMPLES

The explosives samples were obtained from a variety of sources. Commercial blasting explosives such as dynamites were purchased from local blasting distributors. Samples of military explosives were obtained from the 14th Explosives Ordnance Detachment, Ft. Devens, Massachusetts. Laboratory standards of components of military explosives were obtained from the explosives laboratory of the U. S. Army Armament Research, Development and Engineering Center, Dover, New Jersey. Samples of Semtex explosives were obtained from the U.S. Secret Service and the Central Intelligence Agency. Samples of pure nitroglycerine were obtained by extracting a nitroglycerine transdermal medical patch. Pure samples of ethylene glycol dinitrate and diethylene glycol dinitrate were provided by Bureau of Alcohol, Tobacco, and Firearms, Forensic Science Laboratory, Rockville, Maryland. Organic nitro- compounds were obtained from Aldrich Chemical Company, Sigma Chemical Company, Eastman Kodak Company, ICN Chemicals, and were used without further purification.

On receipt of the explosives samples, they were placed in plastic-capped glass vials and stored in large-mouth, screw-capped, plastic bottles. Because dynamite contained ethylene glycol dinitrate and nitroglycerine, both high-vapor pressure compounds, it was not stored with the other explosives to avoid cross contamination.

2.2. ANALYTICAL METHODS

2.2.1 Gas Chromatography-Mass Spectrometry (GC-MS). A Hewlett Packard 5890 gas chromatograph was used with both the Hewlett Packard 5970B Mass Selective Detector and with the Hewlett Packard flame ionization detector. The explosives samples were dissolved in acetone and injected via a micro-liter syringe into the split/splitless injector of the chromatograph. The injector was operated in the splitless mode with the valve closed time of 0.7 min., column head pressure of 50 kPa (10 psi), and total flow of 20 cc/min. The capillary column used was a 30 m J & W Scientific DB-5 column, 0.25 mm diameter, and a 0.25 micron film loading. Isothermal runs were performed with the injector at 145 ° C, the column at 140 ° C, and the mass spectrometer interface at 145 ° C. For the linear-temperature programmed runs, the column was ramped from 40 ° C to

300 ° C, at a rate of 5 ° C/ min. The Hewlett Packard 5970B Mass Selective Detector was operated in the scanning mode and under conditions provided by daily autotunes, using perfluorotributylamine (PFTB). The resulting chromatography peaks were identified by performing a forward/backward library search of the NBS Mass Spectral Library Data Base for each background subtracted mass spectrum.

2.2.2. Gas Chromatography-Flame Ionization Detection (GC-FID) . A second Hewlett Packard model 5890 Gas Chromatograph quipped with a dual flame ionization detector (FID) was used to compare and check Retention Index data previously obtained with the GC-MS. The gas chromatograph was operated as above, with the FID detector operated at 250 ° C. In the FID chromatograms of the explosives, the largest peak was assumed to be that of the explosive.

3. Results

The Isothermal Retention Indices of the explosives, nitro-compounds , and reference compounds are presented Table I; the Linear Programmed Retention Indices are presented in Table II.

4. Discussion

It is apparent that the retention times and retention Indices determined by the two analytical methods do not agree. The retention times of a compound determined by GC-MS differs from that determined by GC-FID because of the transfer line in the mass spectrometer and the vacuum on the ion source and the column; therefore, the retention times by GC-MS will be shorter than by GC-FID, particularly early eluting peaks. Obviously, if the retention times are different, the Retention Indices will be different. The most useful data are therefore those obtained with the GC-FID.

According to Equation (2), the Isothermal Retention Indices should be a linear function of the logarithm of the adjusted retention time. The GC-MS and GC-FID data are plotted in Figure 1, and the first order linear regression line fits the data well. The GC-MS data show some deviation at long retention times; the GC-FID data show some deviation at the shorter retention times. The first GC-FID data point shows the largest deviation, since its retention time is very close to that of the edge of the acetone peak

which was used as the un-retained material. A small error in measurement of either retention time would produce a large error in the calculation of the Retention Index.

Figure 2 presents the GC-MS and the GC-FID Linear Temperature Programmed Retention Indices plotted against the retention time. The lines through the data points are for first order linear regressions and, with a small shift in retention times, would be coincide. There is a deviation from linearity at short retention times; this would be expected, since a small error in a short retention time would produce a larger percentage change in the Retention Index than a small error in a longer retention time. According to Equation (3), the Isothermal Retention Indices should be a linear function of the retention time, and this is evident from the data in Figure 2.

Another test of the "goodness" of the determined Retention Indices is that the Retention Indices should be a linear function of the boiling points for a homologous series of compounds. The boiling points of the nitro-compounds and explosives used in this study are listed in Table III. Figure 3 shows the GC-MS determined Linear Temperature Programmed Retention Indices as a function of boiling point for nitro-paraffins, nitro-aromatics, and selected explosives. Figure 4 shows the corresponding data obtained by GC-FID. The Retention Indices are linear functions of the boiling points for the homologous series of nitro-alkanes and nitro-aromatics. This result indicates that the experimental methodology should yield reliable data of Retention Indices. The boiling points and Retention Indices of four explosives are plotted in the Figures and are represented as triangles. The data points fit reasonably well with the other data, but as can be seen from Table III the actual boiling points of the explosives are difficult to ascertain

5. Conclusions

Linear Temperature Programmed and Isothermal Retention Indices can be determined for explosives molecules using normal hydrocarbons, nitro-alkanes and nitro-aromatics as bracketing compounds. Because of peculiarities in the use of GC-MS, it is recommended that the GC-FID data be used for comparison purposes.

6. Acknowledgment

This work was funded by the Aviation Security Research and Development Service of the Federal Aviation Administration Technical Center.

7. References

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TABLE I
ISOTHERMAL RETENTION INDICES

COMPOUND	GC/MS RETENTION TIME (MIN) DEAD TIME = 1.865	GC/MS RETENTION INDEX	GC/FID RETENTION TIME (MIN) DEAD TIME = 4.240	GC/FID RETENTION INDEX
Acetone (edge)	1.865		4.240	
Nitro-methane	1.916			
Hexane	1.918	600.00	4.247	600.00
Nitro-ethane	1.982	699.58		
Nitro-propane	2.062	765.11		
Octane	2.125	800.00	4.413	800.00
Nitro-butane	2.204	853.48		
Nonane	2.292	900.00	4.597	900.00
Nitro-pentane	2.438	955.13		
Decane	2.593	1000.00	4.822	1000.00
EGDN	2.732	1034.50	5.159	1050.99
Nitro-hexane	2.838	1057.28	5.244	1060.86
Undecane	3.073	1100.00	5.276	1100.00
Nitro-benzene	3.227	1122.69	5.679	1162.48
Dodecane	3.915	1200.00	5.993	1200.00
Tridecane	5.295	1300.00	7.556	1300.00
DEGDN	6.468	1357.28	8.323	1351.13
NG	6.845	1372.91	8.552	1364.54
Tetradecane	7.585	1400.00	9.222	1400.00
Pentadecane	11.399	1500.00	12.734	1500.00
2,4-DNT	14.205	1550.09	15.107	1549.11
Hexadecane	17.822	1600.00	18.267	1600.00
1-Nitro-Naphthalene	19.215	1615.84	19.431	1615.66
2-Nitro-Biphenyl	27.894	1691.22	27.140	1696.33
Heptadecane	28.930	1700.00	27.568	1700.00
2,4,6-TNT	30.844	1714.08	28.435	1707.07
Octadecane	45.832	1800.00	43.272	1800.00
PETN	49.047	1813.94	44.358	1805.54
Nonadecane	74.803	1900.00	68.222	1900.00
RDX	72.142	1891.47	56.497	1859.01
Eicosane	129.301	2000.00	109.432	2000.00

TABLE II
LINEAR TEMPERATURE PROGRAMMED RETENTION INDICES

COMPOUND	GC/MS RETENTION TIME (MIN)	GC/MS RETENTION INDEX	GC/FID RETENTION TIME (MIN)	GC/FID RETENTION INDEX
Acetone (edge)	1.810			
Nitro-methane	2.143			
Hexane	2.286	600.00	4.116	600.00
Nitro-ethane	2.762	636.89	4.850	669.51
Nitro-propane	3.827	719.46	5.558	736.55
Octane	4.866	800.00	6.228	800.00
Nitro-butane	5.863	842.53	6.807	826.02
Nonane	7.210	900.00	8.453	900.00
Nitro-pentane	8.611	946.04	9.085	925.63
Decane	10.253	1000.00	10.919	1000.00
EGDN	11.597	1039.73	12.110	1032.05
Nitro-hexane	11.825	1046.47	12.206	1034.63
Nitro-benzene	13.138	1085.28	13.762	1076.51
Undecane	13.636	1100.00	14.635	1100.00
Dodecane	16.704	1200.00	17.818	1200.00
Tridecane	19.637	1300.00	20.624	1300.00
DEGDN	20.884	1344.19	21.487	1332.85
NG	21.502	1366.09	22.097	1356.07
Tetradecane	22.459	1400.00	23.251	1400.00
Pentadecane	25.142	1500.00	26.117	1500.00
2,4-DNT	26.147	1541.10	26.805	1531.81
Hexadecane	27.587	1600.00	28.280	1600.00
1-Nitro-Naphthalene	27.879	1612.87	28.543	1610.84
Heptadecane	29.856	1700.00	30.706	1700.00
2-Nitro-Biphenyl	29.896	1701.82	30.817	1704.76
2,4,6-TNT	30.244	1717.67	30.908	1708.67
Octadecane	32.052	1800.00	33.037	1800.00
PETN				
Nonadecane	34.217	1900.00	35.027	1900.00
RDX	34.512	1914.76	34.731	1914.09
Eicosane	36.215	2000.00	37.185	2000.00

Table III BOILING POINTS OF NITRO-COMPOUNDS		
COMPOUND	BOILING POINT (°C)	REFERENCE
1-Nitro-methane	101	[4]
1-Nitro-ethane	114	[4]
1-Nitro-propane	130	[4]
1-Nitro-butane	153	[4]
1-Nitro-pentane	173	[4]
1-Nitro-hexane	193	[4]
Nitro-benzene	210	[4]
EGDN	217 (deflagrate)	[5]
DEGDN	246	[5]
NG	256 (explodes)	[5]
2,4-DNT	300 (decomp)	[5]
2,4,6-TNT	300 (deflagrate)	[6]
1-Nitro-naphthalene	304	[6]
2-Nitro-biphenyl	320	[6]
9-Nitro-anthracene	432	[6]

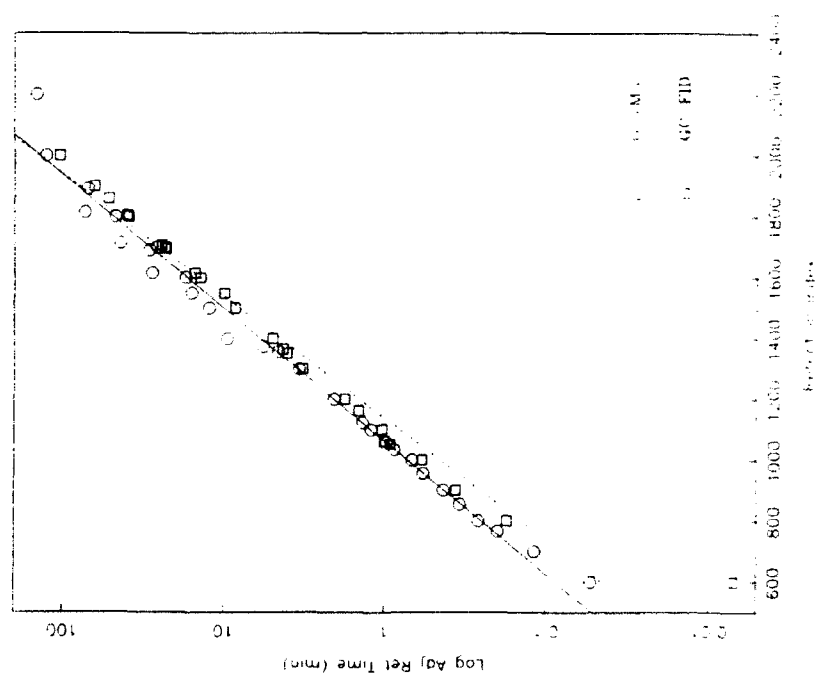


Figure 1. Isothermal Retention Indices vs. Logarithm of the Adjusted Retention Time of Explosives for 30 meter DB-5 Column.

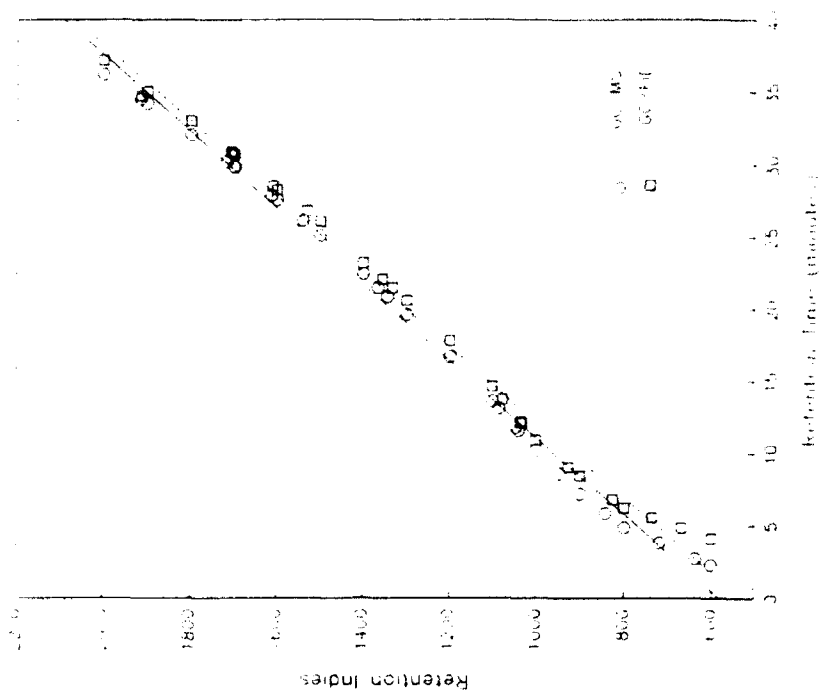


Figure 2. Linear Temperature Programmed Retention Indices vs. the Retention Time of Explosives for 30 Meter DB-5 Column

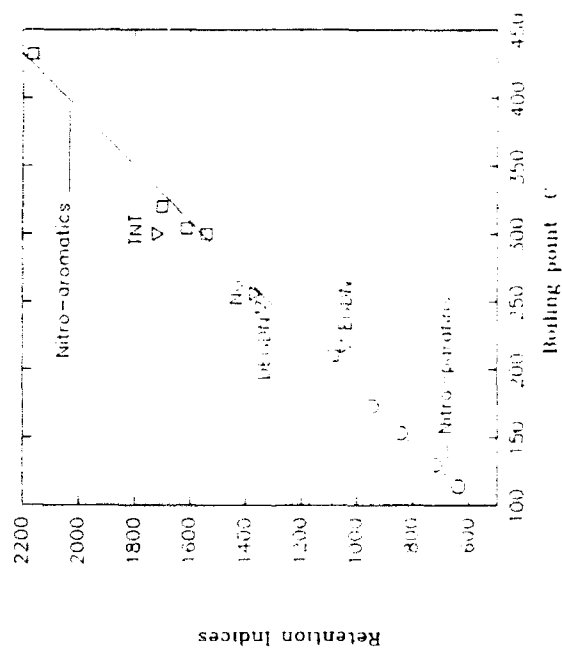


Figure 3. Linear Temperature Programmed Retention Indices vs. the Boiling Points of Homologous Series of Explosives (GC-MS Data).

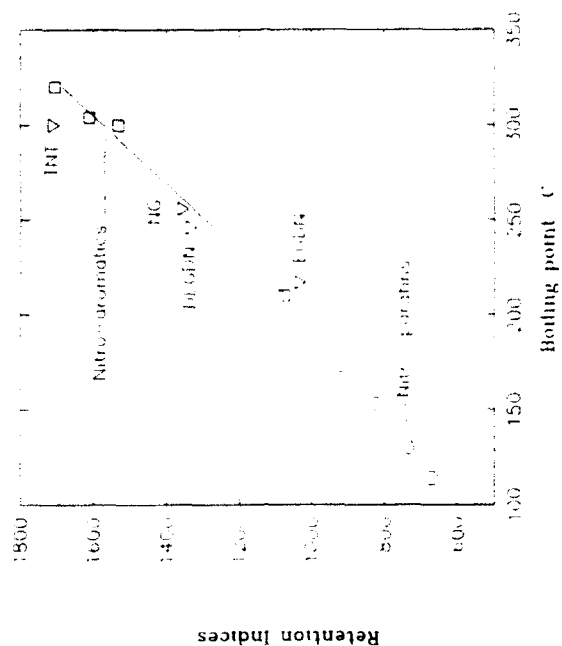


Figure 4. Linear Temperature Programmed Retention Indices vs. the Boiling Points of Homologous Series of Explosives (GC-FID Data).

DETERMINATION OF THE IMPURITY CONCENTRATION PROFILE IN TNT

W. F. ARK AND T. H. CHEN

U. S. Army Armament Research, Development, and Engineering Center Picatinny Arsenal, New Jersey 07806-5000, U. S. A.

ABSTRACT. A rapid direct capillary gas chromatographic procedure capable of determining impurities down to 10 ppm levels in 2, 4, 6-trinitrotoluene (2, 4, 6-TNT) is described.

1. Introduction

Recently, we have conducted a comparative study of the organic impurity concentration profile of 2, 4, 6-TNT samples from two sources by direct capillary gas chromatography employing a bonded silica glass column. This work was conducted to evaluate the suitability and relative merits of both specimens for use in munitions. The objective of this paper is to develop a direct, rapid gas chromatographic method for the intended investigation.

2. Experimental

2.1. APPARATUS

A Hewlett-Packard 5890/5970 Gas Chromatograph/Mass Selective Detector (GC/MSD) was used in the identification of impurities. A Hewlett-Packard 5890A Gas Chromatograph (GC) with a flame ionization detector and a large-bore bonded silica

glass column was employed in the determination of the impurity profiles.

2.2. SPECIMENS AND REAGENTS

2, 4, 6-TNT specimens from two manufacturing sources were Military-Grade. All reagents were Reagent Grade and were used without further purification.

3. Results and Discussion

3.1. IDENTIFICATION OF IMPURITIES

The identification of impurities was necessary prior to quantitative identification. Aside from 4 dinitrotoluene (DNT) and 6 trinitrotoluene (TNT) isomers, m-dinitrobenzene (m-DNB) was found. Figures 1 and 2 show the separation, identification, and confirmation of m-DNB in Sample No. 2. Four other impurities were not identified.

3.2. QUANTITATION

Considerable difficulties were encountered in reproducing the results for impurities at the beginning. This problem was eventually traced to dissolving into and reemission from the bonded phase of minor components. Consequently, this problem was solved by over-loading the column.

Figure 3 shows the gas chromatogram of standard mixtures containing 99.3 wt. % 2, 4, 6-TNT and small quantities of m-DNB, DNT, and TNT isomers. Most impurities were baseline separated except the ones having retention times very close to 2, 4, 6-TNT. Figures 4 and 5 show the gas chromatograms of No. 2 and No.1 specimens, respectively. There are distinctive features for each sample which could be used to identify the origin of the manufacturing source.

This method is capable of determining the concentration of the

impurities down to approximately 10 ppm levels. The reproducibility for all impurities ranges from 10 to 90 ppm.

4. Summary

A rapid, direct gas chromatographic method for the determination of the impurity profile of 2, 4, 6-TNT down to the 10 ppm levels is described. The impurity profile will permit the identification of the source of the sample.

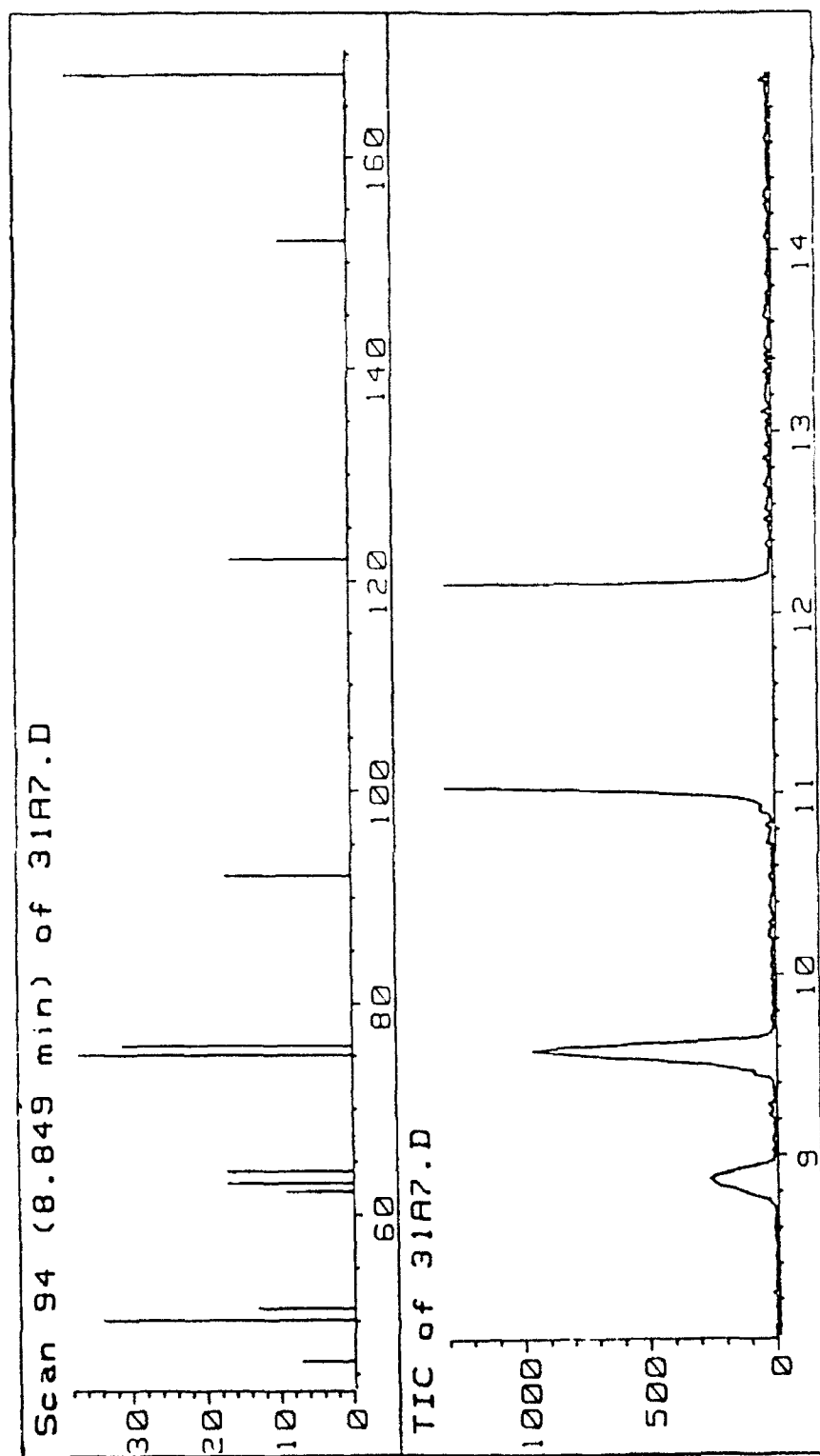


Figure 1. Mass Spectrum (Top) and Total Ion Chromatogram (TIC, Bottom) of Unknown Compound at Scan 94 in the TNT Sample Manufactured in Country No. 2

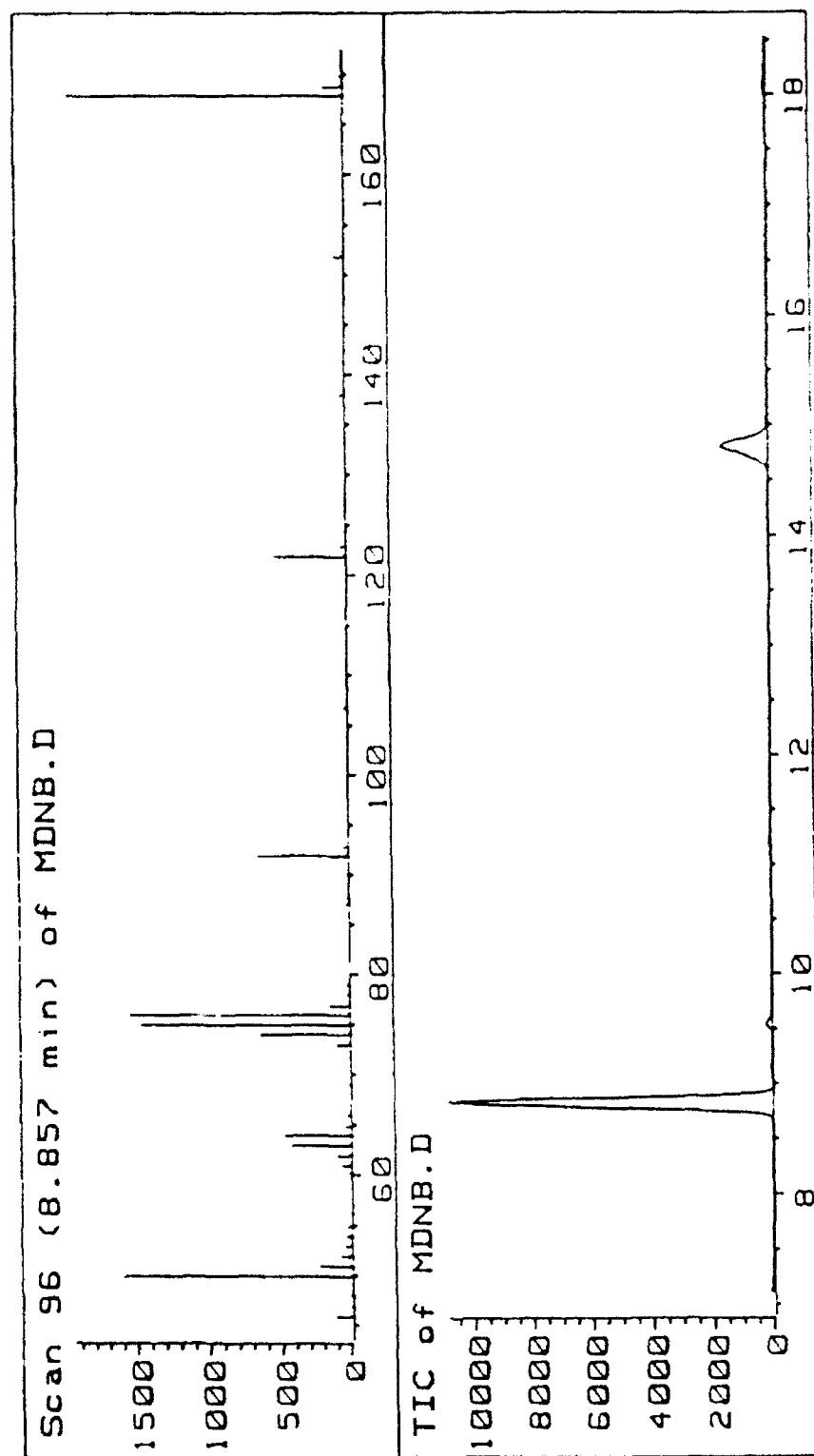


Figure 2. Mass Spectrum (Top) and Total Ion Chromatogram (TIC, Bottom) of Meta-Dinitrobenzene

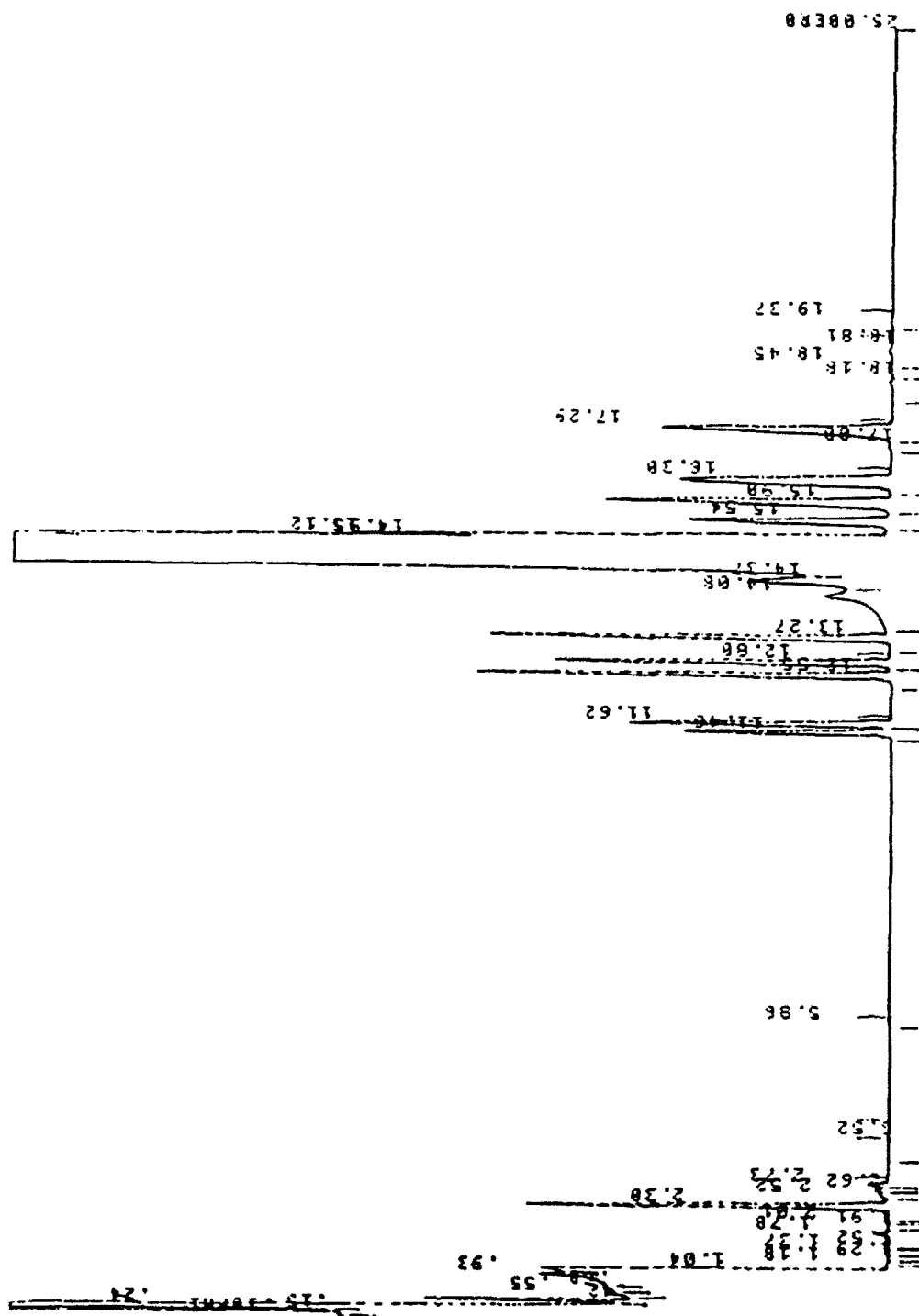


Figure 3. Gas Chromatogram of Standard Mixture Containing Approximately 99.3 Wt. % 2,4,6-TNT, 0.1 Wt. % M-DNB, and 0.1 Wt. % DNT and TNT Isomers in acetone; 1 μ l Injection

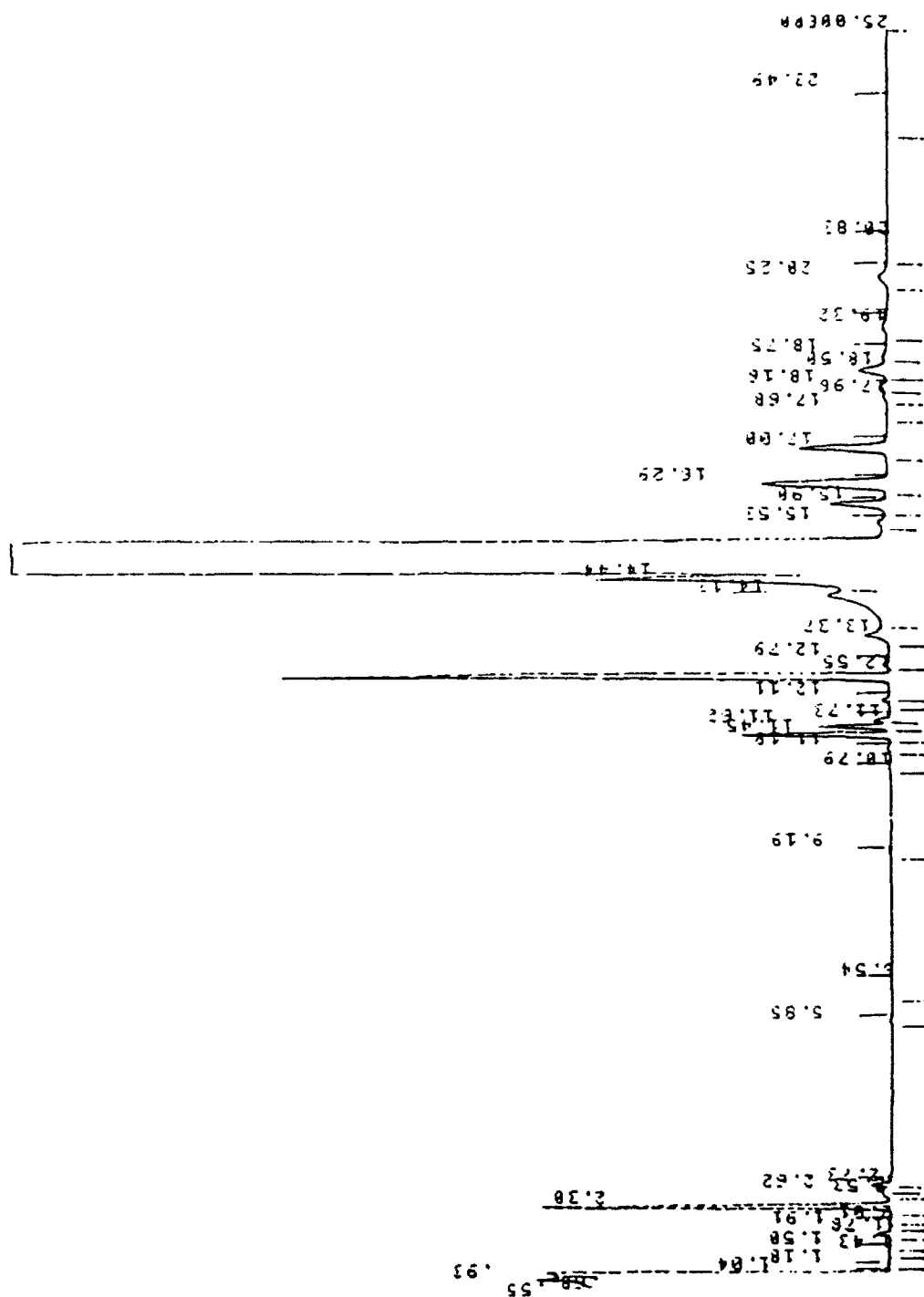


Figure 4. Gas Chromatogram of Approximately 10 Wt. % No. 2 TNT Sample (31B) in Acetone; 1 μ l Injection

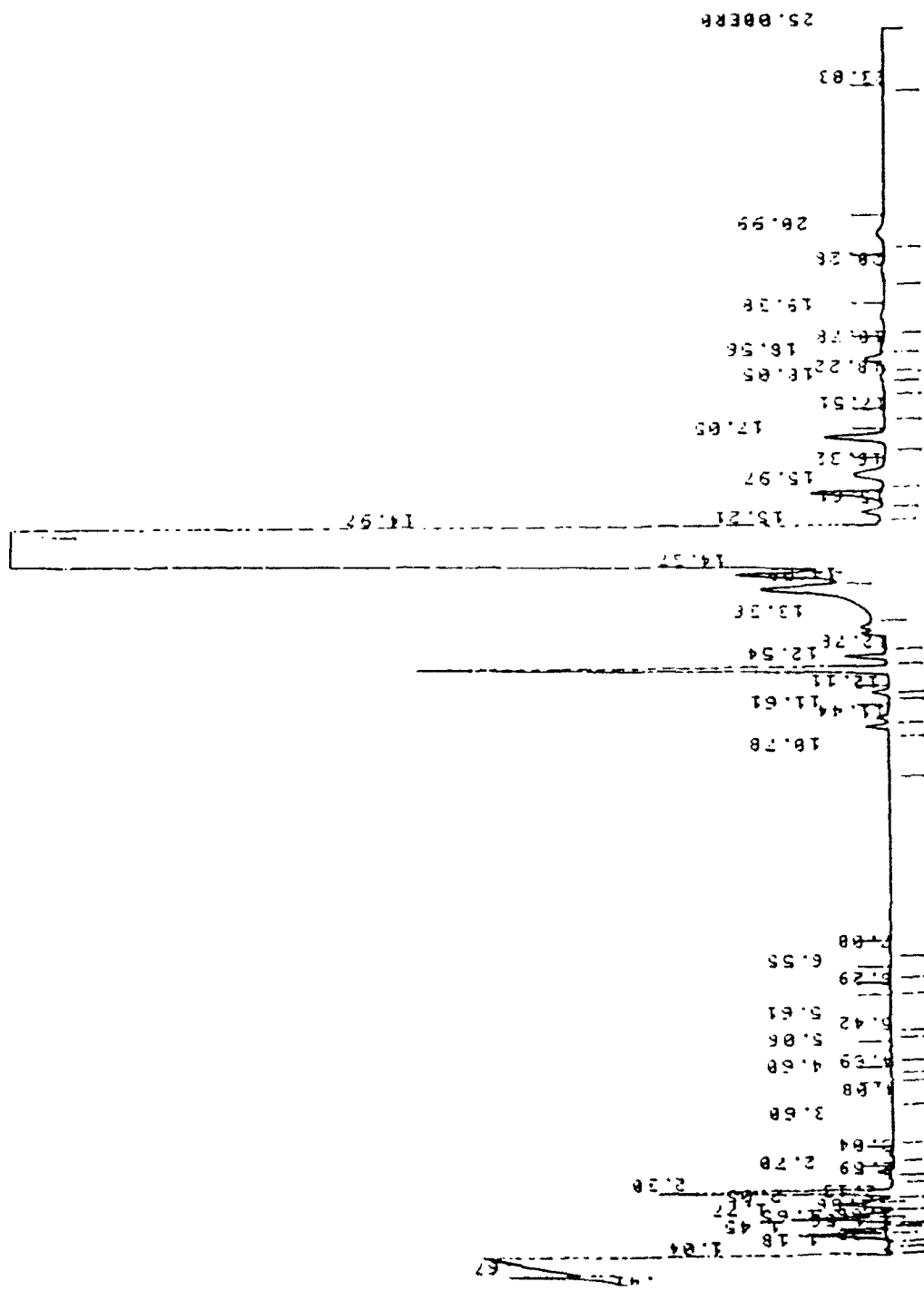


Figure 5 Gas Chromatogram of Approximately 10 wt % No. 1 TNT Sample (Vol-7-897) in Acetone; 1 μ l Injection

INDICATION OF NITROESTER CONCENTRATION IN AIR BY USE OF GAS CHROMATOGRAPHY

J. BIL, A. MARANDA, J. NOWACZEWSKI
Military Technical Academy
01 - 489 Warszawa
Poland

ABSTRACT. The results of measurements of nitroester concentration in air by use of gas chromatography are presented. The factors determining the value of noxious agents concentration are discussed and the usability of the method of gas chromatography is confirmed.

1. INTRODUCTION

Explosives sensitized by liquid nitroesters, such as glycerine trinitrate (TNG) and glycol dinitrate (DNG) are commonly used in the Polish underground mining. The liquid nitroesters escape from the explosives due to a specific vapour pressure and due to the fact, that vapour concentration increases with increasing temperature. These substances penetrate through a respiratory system and skin into blood of human organism causing dangerous phenomena, such as expansion of blood vessels and decrease of arterial pressure [1]. In this paper, the results of measurements of nitroester concentration in air carried out by a method of gas chromatography are presented. Air samples were collected from places of employment with high concentration of glycol dinitrate at a factory manufacturing explosives and from a mine during shot works. On the basis of results obtained, the conditions for harmless work environment at these places were estimated and noxious agents concentrations were also determined.

2. EXPERIMENTAL

To fulfill measurements of nitroester vapour concentration in air, polluted air was sampled first. Next, the investigated substances were separated and an analysis was made. The EMIMAT OH - 602 apparatus manufactured by RADELKIS-METRIMPEX was used to draw air samples (Fig. 1). A basic element of this apparatus is a pump which enables sucking in air with a rate which can be regulated by handwheel (1) within the range from 0 to 60 dm³/h. The flow intensity is read off from three

rotameters. The central rotameter indicates an amount of air going into the apparatus. Left and right rotameters show air volumes flowing through left and right absorption bulbs (3), respectively.

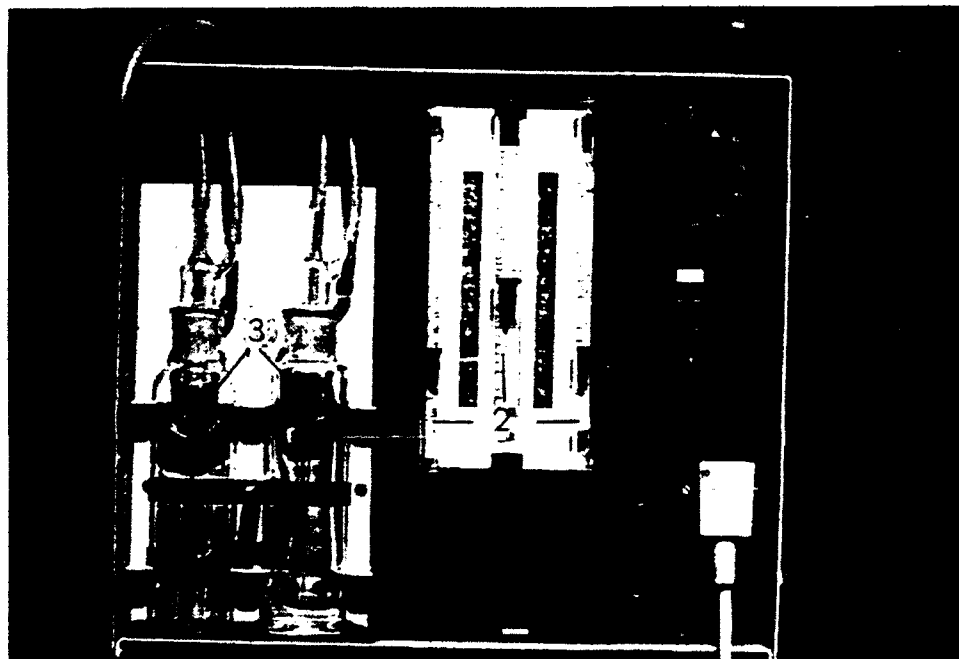


Fig. 1. Air sampling apparatus:
1 - flow control handwheel; 2 - rotameters; 3 - glass absorption bulb (absorbers)

Sucked air flows through a system of glass absorbers (3), in which investigated substances are absorbed. During our experiments these bulbs were not used but a special end - filter packed with silica gel was located at the end of the sucking hose (Fig. 2).

This replacement was made to meet the requirements of the PN-89/2-042121 and PN-89/2-04213/02 Polish standard specifications describing the way of air sampling.

Subsequently, the absorbed nitroesters were washed out from the silica gel by ethyl alcohol and the obtained extracts were analysed by a Pye Unicam gas chromatograph. It had an electron capture detector and a glass column of 1.8 m length and 4 mm I. D. with N-AW-DMCS Chromaton being the carrier of the Carbowax 20M (10% by wt). The dispersity of the carrier was of 80/100 mesh. Before the analysis of the investigated solutions, vapour concentration of nitroesters was determined in the standard alcoholic solutions consisting of ethyl alcohol and liquid nitroester with the specified concentrations. The chromatographic analyses of glycol dinitrate and glycerinetrinitrate were performed at temperatures of 125°C and 180°C, respectively. The flow of carrier gas (argon) through column was of 72,3 cm³/min.

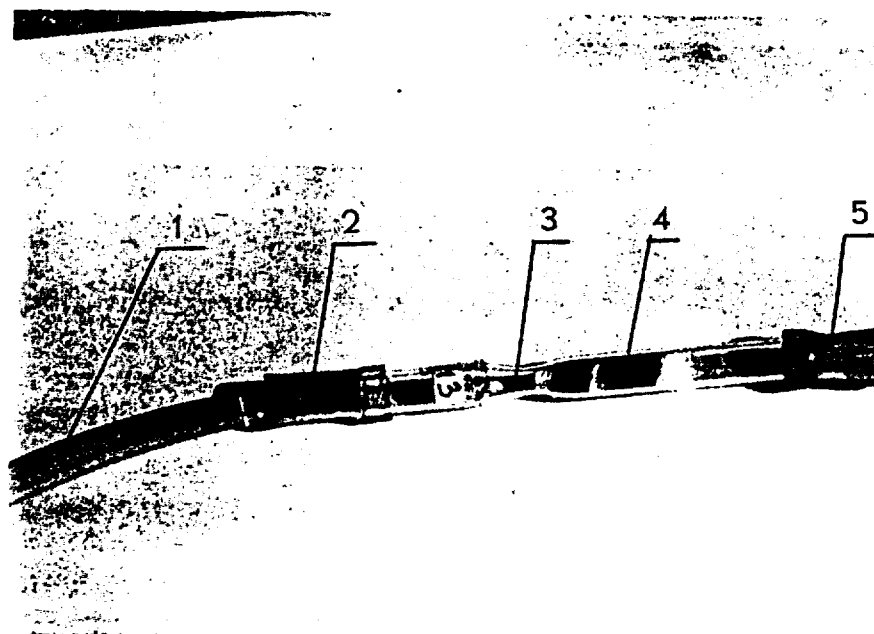


Fig. 2. End of air - sucking hose:

1 - hose; 2 - elastic junction; 3 - glass pipe of absorber;
4 - silica gel; 5 - elastic junction to close the absorber pipe.

The obtained chromatograms were compared with those found for reference solutions and thus the concentration of nitroesters in the investigated samples was determined.

3. INDICATION OF NITROESTER CONCENTRATION IN AIR IN PLACES OF EMPLOYMENT

The air samples were collected from an explosive department while the D-12G5H dynamite was being manufactured. All measurements were performed with a volumetric flow rate of air of $2 \text{ dm}^3/\text{min}$ and a flow duration of 5 minutes. The sampling was made in the rooms with the presumable highest vapour concentration, where workers most often complained to arduous work environment. The room of dynamite stick manufacturing (D-1), the room of dynamite mass mixing (D-2) and the storage of dynamite pulp (D-3) were tested. The samples 1 and 2 were taken from D-1 when a stick manufacturing machine was working. The samples 3 and 4 were drawn from D-2 during mixing and the samples 5 and 6 after mixing of dynamite mass. The samples 7 to 9 were taken from D-3 during storage of different pulps. Thus, the samples 7, 8 and 9 were drawn from the space over containers with the 12G5H dynamite, the 10G5H dynamite and the 9GS dynamite, respectively. Chemical constitution of the investigated dynamites are given in table 1 and the results of concentration measurements of glycol dinitrate and glycerine trinitrate are shown in Table 2.

Table 1. Chemical constitution of some dynamites

Component	Weight content, wt %		
	D - 9G5	D - 10G5H	D - 12G5H
Ammonium nitrate	60.0	60.0	58.5
Sodium nitrate	8.0	2.0	6.0
Glycerine trinitrate	6.0	5.0	5.0
Glycol dinitrate	18.0	20.0	20.0
Dinitrotoluene	6.0	5.0	4.0
Nitrocellulose	0.9	0.8	1.0
Wood flour	1.0	0.6	1.0
Ferric oxide	0.1	0.1	0.1
Barium sulfate	-	5.0	3.0
Guar gum	-	1.0	-
Dextrin	-	-	0.4
Slack wax	-	-	1.0
Calcium stearate	-	0.5	-

Table 2. Results of analysis of air samples from dynamite department

Sample number	Concentration in air, mg/m ³	
	DNG	TNG
1.	0.225	0.150
2.	0.230	0.160
3.	1.200	0.220
4.	1.100	0.240
5.	0.900	0.200
6.	0.800	0.190
7.	0.760	0.280
8.	2.400	0.560
9.	0.700	0.120

4. INDICATION OF NITROESTER CONCENTRATION DURING SHOT WORKS IN MINE

The investigations were carried out on the drawing level of 375 meters at an ambient temperature of 27 to 27.5 °C during driving at forehead, by loading of dynamite and after detonation of 240 kg charge of the

D-12G5H dynamite, while outer air was blown in with an intensity of 340 m³/min. Air sample 1 was drawn before loading of coal face and sample 2 drawn from the space above containers with explosives. Samples 3 and 4 were taken after loading from points located at a distance of 5.5 m and 1.5 m, drawn at a distance of 3 m from output longwall 60 minutes after shot and from above the output of air flow. The results of chromatographic analysis of the DNG and TNG concentration in air are presented in Table 3.

Table 3. Results of analysis of air samples from mining

Sample number	Concentration in air, mg/m ³	
	DNG	TNG
1.	0.06	0.12
2.	1.04	0.21
3.	0.17	0.07
4.	0.18	0.05
5.	2.19	0.54

5. ANALYSIS OF THE RESULTS

From the results summarized in tables 2 and 3 it is inferred that concentration of TNG vapour is below 0.5 mg/m³ with the exception of two cases. The concentration of DNG vapour is generally higher as compared with that of TNG vapour. These results correspond with expectations due to the fact that the content of DNG in dynamites is higher than that of TNG, and hence the vapour pressure of DNG is also higher than that of TNG [2]. The vapour pressure of DNG in air exceeds the permissible limit of 1.5 mg/m³ in Poland. No correlation is observed between the content of particular dynamite components and the concentration of nitroesters in air. However, the positive influence of nitrocellulose on the nitroester concentration can be observed as nitrocellulose brings about an increase in viscosity of the nitroesters, thus hindering their evaporation. The higher vapour concentration of nitroesters during dynamite mixing, as compared with that during its loading, is due to the evaporation surface being large during dynamite homogenization.

Very interesting results of analysis were obtained for the air samples drawn from heading before shot works (sample 1 in Table 3). The concentration of nitroester vapour, especially that of TNG, was found to be significant compared to the environmental background. This phenomenon is probably caused by the desorption of nitroesters absorbed earlier by rock-massif during incomplete reaction of dynamites in blast-holes. The incompleteness of reactions occurring during dynamite detonation is also confirmed by the high content of nitroesters in samples drawn after shot (sample 5 in table 3). In our opinion, the results of investigations,

confirm usability of the presented chromatographic method because it enables to determine the content of nitroesters vapour within the wide concentration range from 0.025 to 2.4 mg/m³ (table 2). The measurements are not disturbed by other pollution in air, and therefore, precise and repeatable results are obtained.

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The Instrumental Analysis of Intact and Post Blast Water Gel and Emulsion Explosives

E.C. Bender, J. Crump, C.R. Midkiff, Jr.

*Forensic Science Laboratory, National Laboratory Center, BATF, Rockville, Maryland;
Michigan State University, East Lansing, Michigan and Forensic Science Laboratory,
National Laboratory Center, BATF respectively.*

ABSTRACT: The production of water gel and emulsion explosives is gradually replacing nitroglycerin dynamites. Due to their increased use in criminal activity it is important that the forensic explosive examiner have a scheme for the analysis of these types of materials. Presented here is a procedure for the instrumental analysis of emulsions and water gels both before and after detonation.

A pre-blast approach to separate these explosives into their basic components for analysis is discussed. The ingredients include oxidizers, alkyl amine nitrates, oils/waxes, gelling agents and various other additives.

A scheme for post blast recovery, purification and identification of water gel and emulsion components is described.

Introduction

The increased use of water gel and emulsion explosives demands that the explosive examiner have a systematic approach to their analysis. Water gels usually consist of a mixture of water, oxidizer(s), fuels, ie. aluminum, and a gel which binds the formulation together, eg. guar gum. Microballoons are added to adjust the sensitivity and density of the water gel.

Emulsions differ from water gels in that they have, in addition to the above listed ingredients, an oil/wax and emulsifier mixture. This is used in place of the gelling agent to hold the ingredients together and provide structural integrity.

Equipment and Conditions

The gas chromatograph used was a Perkin Elmer 8500 equipped with a program temperature vaporizer (PTV) injector and a flame ionization detector (FID). The column was a 15 meter, .25mm i.d. Quadrex aluminum clad fused silica capillary with a .1 micron methyl silicone film. Hydrogen was the carrier gas which was held at a head pressure of 15 psi and split 10:1. The oven initially was held at 100°C for 5 minutes then heated to 420°C at 10°C per minute. The PTV was heated ballistically to 430°C and held for 4 minutes. The FID was set to 450°C.

The trinitrobenzenesulfonic acid (TNBS) derivatives were prepared from a water extract of the sample. Approximately 1 milliliter of sample was placed in a one dram vial with 1 milliliter of 4% NaHCO₃ and .5 milliliters of a .1% TNBS solution. The vial was placed in an oven set at 50°C for one hour. The derivative which was formed was extracted from the reagent with benzene. The benzene was dried with anhydrous sodium sulfate before HPLC analysis [1].

The High Performance Liquid Chromatograph (HPLC) used was a Hewlett Packard model 1090 with model 7010 Rheodyne injector fitted with a 5 microliter loop. The effluent stream was monitored with a Waters Associates Model 440 absorbance detector at 340 nanometers. The column was a Whatman 4.6mm x 25cm, Polar Amino Cyano (PAC). The solvent system consisted of the following: A - 65% iso-octane, 30% methylene chloride, 5% isopropanol; B - 60% iso-octane, 30% methylene chloride, 10% isopropanol. The solvent program started at 0%B and went to 100%B in 10 minutes. The solvent flow was 1.0 milliliter per minute [1].

A Dionex Bio-IC was used to analyze the ion and sugar components of the sample. A Dionex CarboPac PA1 column with an eluent of 15mM NaOH at a flow of 1.0 milliliter per minute was used for the sugars. A pulsed amperometric detector (PAD) monitored the effluent. To enhance detector performance 200mM NaOH was added post column at 1.0 milliliter per minute [2]. A Dionex IonPac CS12 column was used to do the cation analysis. The eluent was 20mM HCL pumped at a flow of 1.0 milliliter per minute. A Dionex CMMS-II micromembrane suppressor was used which was regenerated with 100mM TBAOH [3]. The anions were analyzed on a Waters Associates IC-PAK Anion HC column [4]. The solvent system was a sodium hydroxide gradient consisting of the following: Solvent A - 5% Acetonitrile in water; Solvent B - 33mM NaOH in 5% Acetonitrile. The gradient started at 10%B for 4 minutes, then increased to 90%B at 10 minutes with a five minute hold.

Samples were homogenized with a Biospec Tissue Tearor.

All organic solvents were Burdick & Jackson distilled in glass. The water used was from a Barnsted purification system.

The Amberlite IRN-150 L/C resin was purchased from Supelco Separation Technologies.

Experimental

The emulsions which were used in the analysis were all cap sensitive explosives. These types of emulsions would be the most likely encountered by a forensic explosive examiner. Samples of approximately ½ gram were used in each pre-blast analysis. Initially the emulsions were extracted with iso-octane and broken up with a homogenizer. The extract was filtered, and the supernatant analyzed by high temperature gas chromatography (HT-GC). The extract contained the oil/wax and emulsifier mixture.

Figure 1 illustrates the chromatogram obtained from Powermax 440 manufactured by Imperial Chemical Industries (ICI). Although the oil/wax combination dominates the chromatogram, the emulsifier can still be identified. The emulsifying packages varied widely among the samples tested. Examples of this can be seen in Figures 2 and 3.

Figure 1.

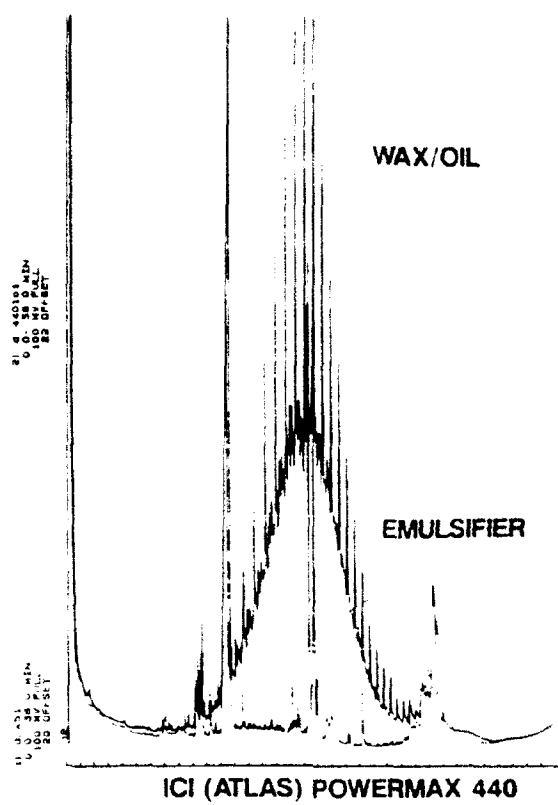


Figure 2.

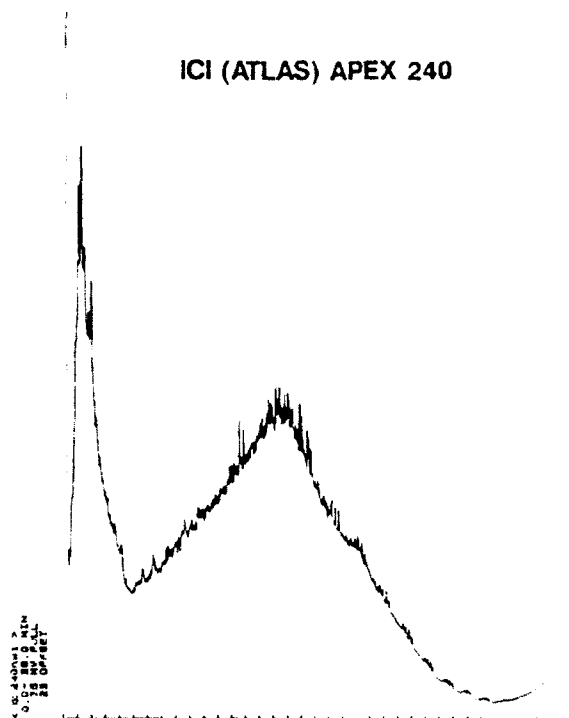
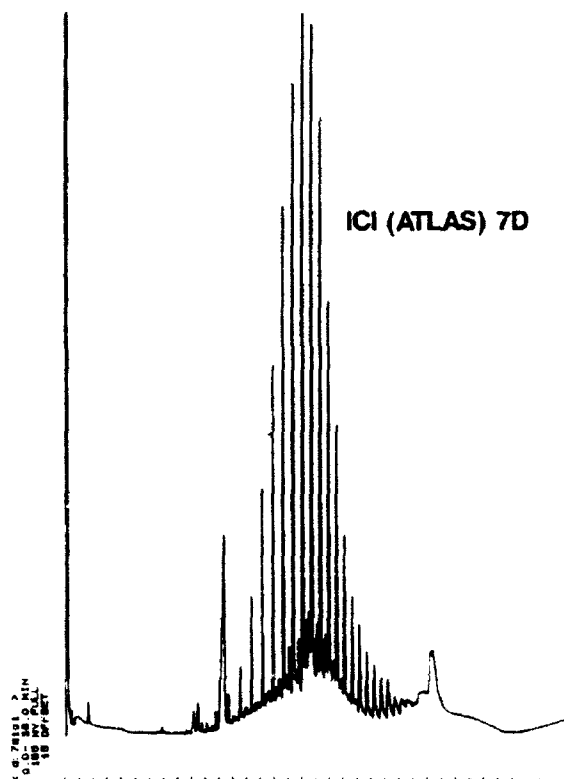


Figure 3.



The insoluble fraction would contain the oxidizers, microballoons, and aluminum. The oxidizers were removed by a water extraction, filtered, and subsequently analyzed by ion chromatography. Both anions and cations were examined. If the emulsion contains an alkyl amine nitrate, a portion of the water extract should be derivatized by TNBS. For Example, the ICI emulsion "7D" contains ethylenediamine dinitrate which is unique to this formulation. This compound was converted into its trinitrobenzenesulfonic acid derivative and analyzed by HPLC. The chromatogram is shown in Figure 4. In addition to the ethylenediamine, ammonia (from ammonium nitrate and perchlorate) was also present.

The remaining material, consisting of the microballoons and possibly aluminum, was mounted on a stub and analyzed by a scanning electron microscope (SEM) with attached energy dispersive spectrometer (EDS). The microballoons were visualized by the SEM and the elemental analysis of the aluminum was performed by the EDS. A schematic for the pre-blast analysis of emulsions is given in Figure 5.

Figure 4.

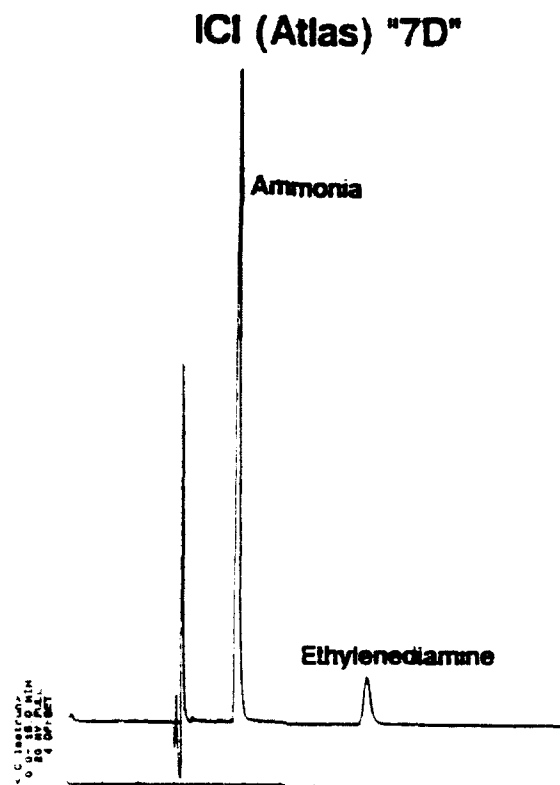


Figure 5.

EMULSIONS		
ISO-OCTANE		
INSOLUBLE		SOLUBLE
	H ₂ O	
SOLUBLE	INSOLUBLE	HT-GC
ION CHROMATOGRAPHY	SEM	OIL/WAX
ANIONS	MICROBALLOONS	
CATIONS	ALUMINUM	EMULSIFIER

The post blast analysis of emulsions was generally the same as the above procedure. A cartridge of ICI "Powermax 440" was detonated on a soil surface. The soil from the blast crater was collected and extracted with iso-octane. When the solid was placed in the solvent a number of microballoons floated to the surface. These were removed with a glass rod and visualized by SEM. The extract was passed through a Supelco LC-SI SPE tube to remove any polar material and analyzed by HT-GC. The chromatogram is illustrated in Figure 6. The soil was then extracted with water and analyzed by IC. The chromatogram of the anions in this extract are in Figure 7. The water extract was also derivatized with TNBS for the detection of the ethylenediamine.

Figure 6.

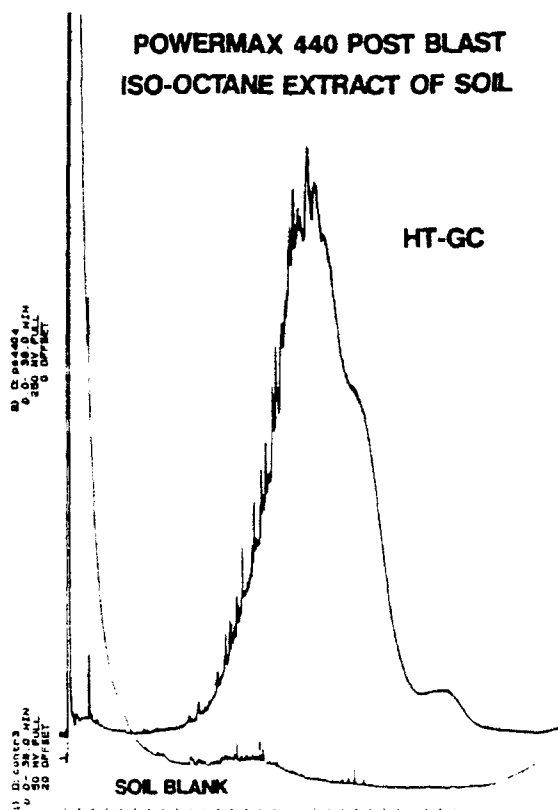
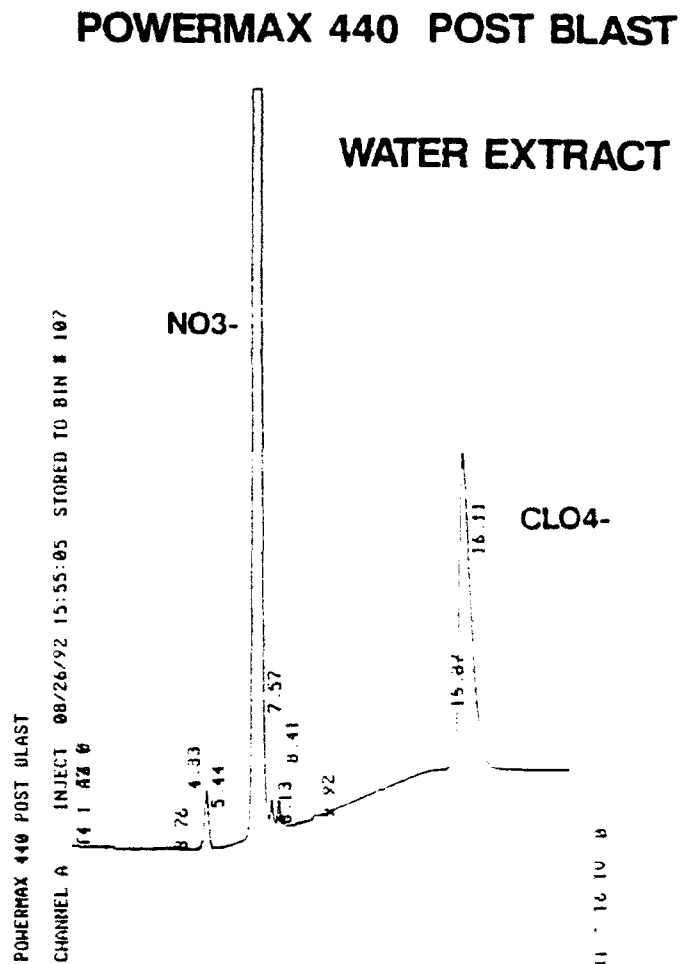
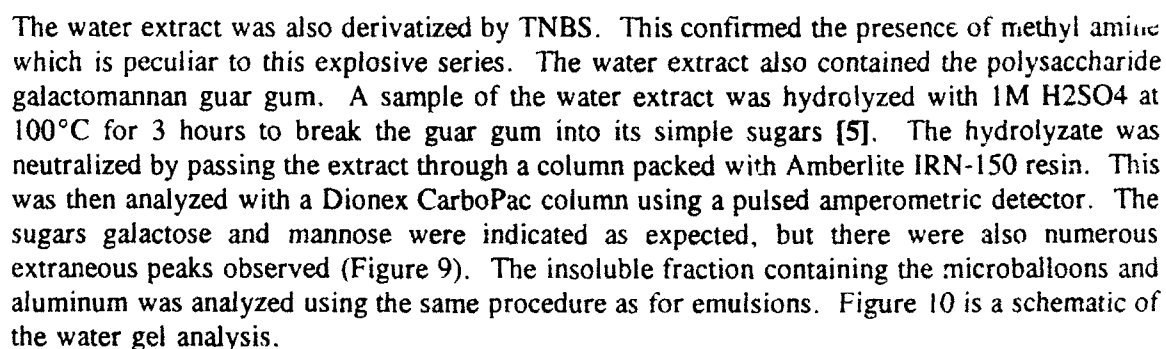


Figure 7.



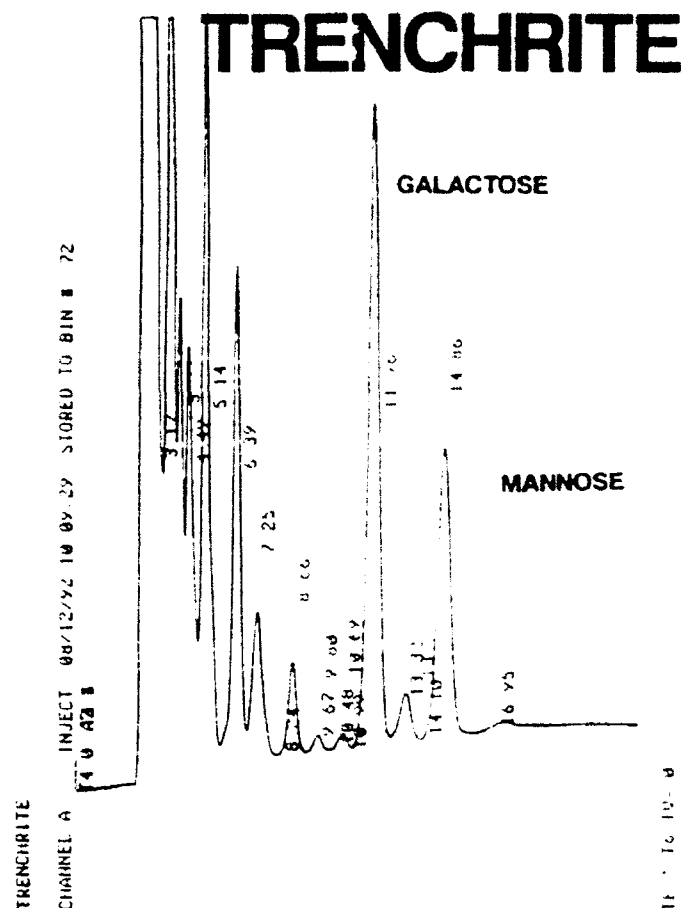
The only water gel examined in this study was "Trenchrite", which is manufactured by Explosives Technologies International (ETI).. This explosive consists of water; sodium, ammonium, calcium and methyl amine nitrates; aluminum; microballoons and the gelling agent guar gum.

The gel was broken down by homogenizing for a few minutes in water. This water fraction contained all the nitrates and the gelling agent. The water solution again was analyzed by IC. The cations are shown in Figure 8.



The post blast analysis of the water gels is the same as the emulsions because the discrimination of blast effects between the two is usually not possible.

Figure 9.



Conclusion

Water gel and emulsion explosives will be more frequently encountered by the forensic explosive examiner. A systematic approach should make their analysis more manageable. These types of explosive compositions will however, present a formidable challenge to the analyst after detonation. This is because many of the components have applications other than for explosives. An example of this is ammonium nitrate. It is not only found in emulsion, water gels, dynamite, ANFO, etc. but also in fertilizers and cold packs. The successful post blast identification of a water gel or emulsion will depend on sample matrix control. It may also require the identification of a combination of ingredients.

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CHARACTERISATION OF COAL-MINING EXPLOSIVES BY CLASSICAL WET ANALYSIS AND MODERN INSTRUMENTAL ANALYSIS

H. Köhler
Dynamit Nobel AG
Werk Schlebusch
Kalkstrasse 218
W-5090 Leverkusen 1
Germany

ABSTRACT. Permitted explosives for coal-mining are mainly mixtures of two or three inorganic salts and nitrate esters e.g. glyceroltrinitrate and glycoldinitrate with minor other components. According to German laws these explosives must always be produced in the same composition within very tight limits. Full analysis of the products is essential for quality control and for fulfilling the legal requirements. At the first thought, exact quantitative analysis of the mixtures of a few inorganic salts seems to be simple, but it isn't. This contribution gives full details of analytic methods, both classical wet and instrumental.

Calculation examples and description of used apparatus will also be presented.

Having methods for full quantitative analysis of these explosives can be helpful for identification of types, origin and manufacturer of these special explosives because of their registered and therefore known composition.

1. INTRODUCTION

Powdery explosives for coal-mining, especially those for use in coal-mines where fire damp/air mixtures can be present, are mixtures of inorganic salts, e.g. sodium nitrate, ammonium nitrate, ammonium chloride and organic nitrates, e.g. glyceroltrinitrate and glycoldinitrate. In addition are present small quantities of calcium carbonate, metal salts of fatty acids and waterproofing agents like guar powder or wheat flour. (1)

Explosives manufactured in the territory of the Federal Republic of Germany are registrated and permitted by the german 'Sprengstoffgesetz' (Explosives Law).

Explosives for the coal-mining are additionally regulated and controlled by local coal-mining authorities. For the manufacturers of explosives it is therefore necessary to produce materials, which are in compliance with these regulations.

The produced explosive materials must have the same composition as the first registrated and permitted samples. The productions must be controlled by analysis of the manufactured material to determine the correct composition.

Though at the first glance the analysis of the mixture of the few inorganic salts seems to be simple, it is not so easy in practical work because of the mutual influence of the salts with each other and the other components. (3)
The following contribution describes methods which are used for the characterisation of explosive materials for coal-mining.

Table 1 gives a qualitative overview of the three types of coal-mining explosives.

Table 1

Type A	Type B	Type C
Nitroglycerin	Nitroglycerin	Nitroglycerin
Ethylenglycol-dinitrate	Ethylenglycol-dinitrate	Ethylenglycol-dinitrate
NH ₄ Cl	NH ₄ Cl	NH ₄ Cl
KNO ₃	NaNO ₃	NH ₄ NO ₃
		NaNO ₃
CaCO ₃	CaCO ₃	CaCO ₃

2. EXPERIMENTAL

The characterisation of permitted explosives is performed under two different aspects: Routine control of each batch and full analysis as random test for statistical quality control.

This work is done by a combination of classical wet analysis and modern instrumental analysis.

2.1. ROUTINE CONTROL

Analysis of each batch (one batch = 250 kg, ca. 150 batches per day) involves the determination of nitrate ester, water content and content of ammonium chloride.

The content of glyceroltrinitrate/glycoldinitrate is determined by photometric method by UV-absorption at 283 nm.

Five grams of explosive are shaken with 50 ml ethylacetate in an erlenmeyer flask for ten minutes. After filtration the clear solution passes the flow-cell of the photometer. The content is displayed on the instrument panel in percentage of the nitrate esters. It is very important that this photometric method is calibrated with a standard explosives mixture prepared in the laboratory.

Calibration with pure nitrate ester-solution in ethylacetate gives not the correct results. The reason for this is the solubility of UV-absorbing substances from the other ingredients of the explosives.

The accuracy of the photometric method is within the limits of the specification. The method is fast enough for the analysis of 150 to 200 batches per eight hours.

Water content is determined by Karl-Fischer method, using the K.F. titrator E 452 with K.F. solution Merck 9248, dissolving five grams of explosives in 15 ml methanol.

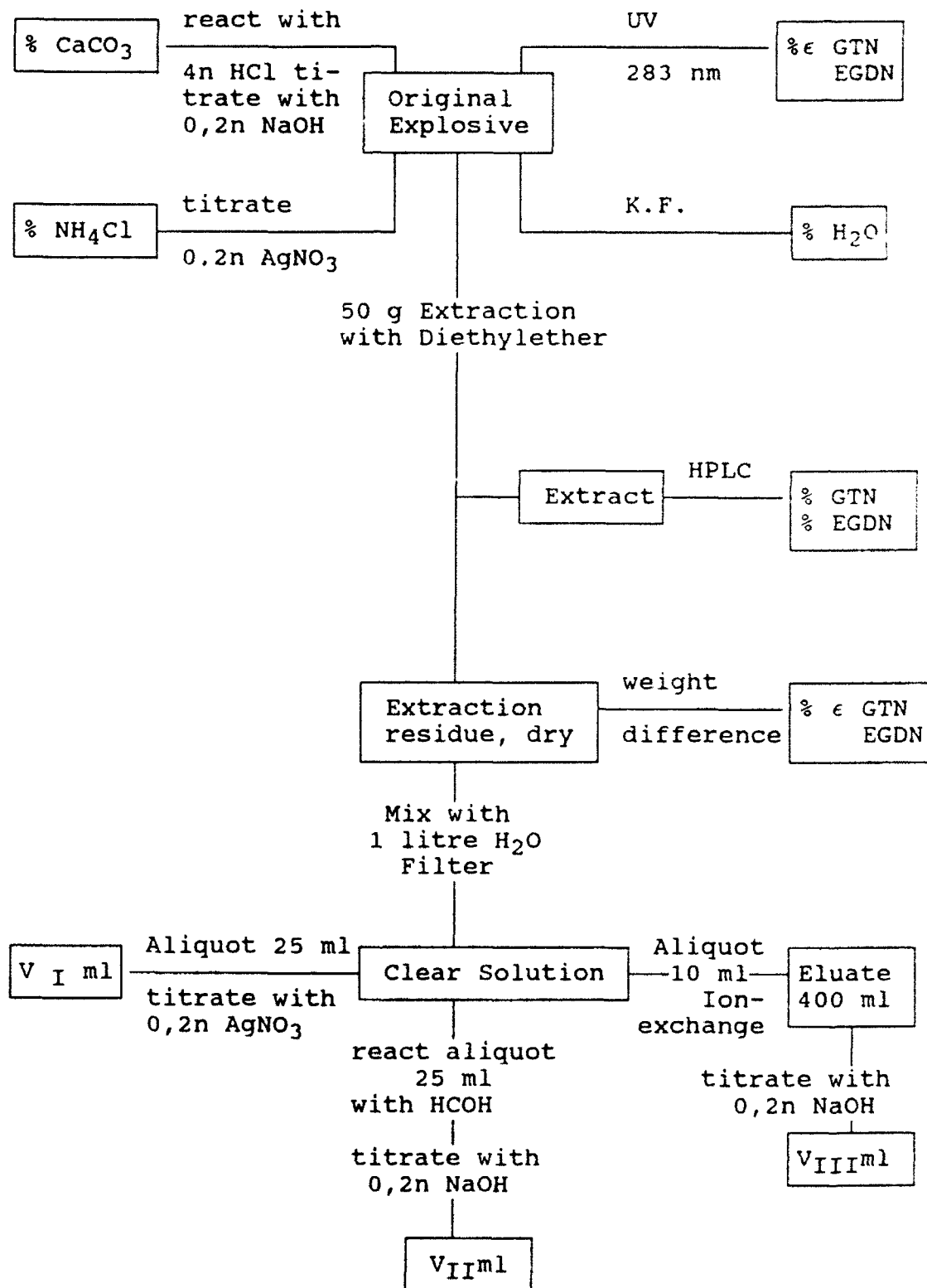
Content of ammonium chloride is determined directly in the original sample by argentometric titration. 250 mg are wetted with one ml methanol in a 150 ml glass beaker, 90 ml water are added and then titrated with 0,1 n silver nitrate solution. We use instrumental potentiometric titration equipped with a special silver/silver nitrate electrode.

2.2. FULL ANALYSIS

Random test of the explosives is more time-consuming than the methods described above. In the following the analysis of the most complex explosive with a mixture of three inorganic salts (ammonium chloride, ammonium nitrate and sodium nitrate) is described.

The steps for doing the analysis are given in the flow diagram on the next page:

FLOW DIAGRAM

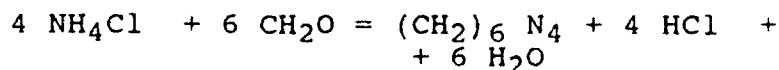
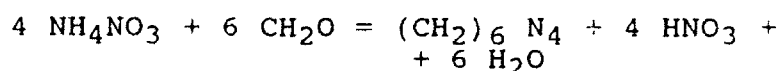


50 grams of sample are extracted four hours in a soxhlet apparatus with diethylether on a steam bath. After extraction the remaining residue is heated for 3 hours in a drying oven at the temperature of 343 K. The weight of the dried material corrected with the previous determined water content gives the content of the sum of the two nitrate esters. This value can be controlled by weighing the solvent freed extract. Evaporating the ether is carried out at room temperature under a hood.

The extract of the explosive is a mixture of glyceroltrinitrate and glycoldinitrate. The ratio of the two nitrate esters is determined by high pressure liquid chromatography. This analysis is performed on reversed phase C-18 columns with acetonitrile/water mixture 1 : 1 by volume. Detection is by UV at 210 nm. The flow rate is 1 ml per minute. Glyceroltrinitrate elutes after 5,2 minutes, glycoldinitrate after 3,6 minutes. Calibration is done by the external standard method with the pure nitrate esters. (2)

The following steps of analysis are carried out with the dried extraction residue. The total amount of the residue is transferred into a 1 litre volumetric flask, distilled water is added to the mark and the mixture is vigorously shaken. Then the mixture is poured through a big fluted filter. Filtration is quick enough to obtain ca. 700 ml of a clear solution. 25 ml of this solution are titrated with 0,2 n silver nitrate solution using the titroprocessor. V_I in ml is the required volume of 0,2 n AgNO_3 and is calculated as content of ammonium chloride.

Another aliquot of 25 ml is reacted with 15 % formaldehyde-solution to form nitric and hydrochloric acid by the reaction of ammonium to hexamethylenetetramine.



Titration with 0,2 n sodium hydroxide solution against phenolphthalein-indicator results in the value for total acidity. The required volume of 0,2 n NaOH for neutralization is V_{II} (ml). From the difference of $V_{II} - V_I$ the content of ammonium nitrate is calculated.

For the determination of sodium nitrate, the third salt in the mixture, an ion exchange method is used. We use the ion exchange resin type 'Lewatit - S 100' which is a sulphonated type in its acidic form. This resin has been regenerated before analysis with a 5 % hydrochloric acid solution.

An aliquot of 10 ml is poured on top of the ion exchange column. The column is washed with distilled water. The ion exchange is complete when ca. 400 ml have been eluted. The whole eluate is titrated with 0,2 n sodium hydroxide solution. Phenolphthalein is used as indicator. The required volume of 0,2n NaOH for neutralization is V_{III} (ml). With this value the content of sodium nitrate can be calculated.

The determination of calcium carbonate is carried out with the original sample of explosives material. The principle of analysis is reaction of calcium carbonate with an excess of 4 n hydrochloric acid and retitrating the surplus of acid.

5 gram of explosive are reacted for 30 minutes with 5 ml 4 n hydrochloric acid in a 250 ml volumetric flask. Then the flask is filled with distilled water to the mark. After quick filtration through a fluted filter, an aliquot of 25 ml is titrated with 0,1 n sodium hydroxide solution with methyl orange as indicator. The colour changes from red to yellow.

The methods described above are not applicable for explosives which contain a mixture of sodium nitrate and potassium nitrate. In this case the cations must be determined by other methods, such as flame photometric analysis or ion chromatography.

These two methods could also be an alternative for the classical ion exchange. Our experience has shown that due to the high sensitivity of the two methods the samples have to be diluted extremely. Therefore the results are not satisfactory in regard of accuracy.

The full analysis of the explosives with the combination of only two inorganic salts ($\text{NH}_4\text{Cl}/\text{KNO}_3$ = type A or $\text{NH}_4\text{Cl}/\text{NaNO}_3$ = type B) is performed in the same way as described for type C, only the step of the formaldehyde reaction is omitted.

2.3 Calculation example for type A:

$$\% \text{NH}_4\text{Cl} = 2 \times \frac{V_I \times 0,2 \times 53,5 \times 40}{1000}$$

$$\% \text{KNO}_3 = 2 \times \frac{(V_{III} \times 2,5 - V_I) \times 0,2 \times 101,1 \times 40}{1000}$$

V_I = ml 0,2 n silver nitrate solution
 V_{III} = ml 0,2 n sodium hydroxide solution
 (ion exchange method)

Molecular weights : $\text{NH}_4\text{Cl} = 53,5$
 $\text{KNO}_3 = 101,1$

2.4 Calculation example for type B :

$$\% \text{NH}_4\text{Cl} = 2 \times \frac{V_I \times 0,2 \times 53,5 \times 40}{1000}$$

$$\% \text{NaNO}_3 = 2 \times \frac{(V_{III} \times 2,5 - V_I) \times 0,2 \times 85 \times 40}{1000}$$

V_I = ml 0,2 n silver nitrate solution
 V_{III} = ml 0,2 n sodium hydroxide solution
 (ion exchange method)

Molecular weights: $\text{NH}_4\text{Cl} = 53,5$
 $\text{NaNO}_3 = 85$

2.5 Calculation example for type C:

$$\% \text{NH}_4\text{Cl} = 2 \times \frac{V_I \times 0,2 \times 53,5 \times 40}{1000}$$

$$\% \text{NH}_4\text{NO}_3 = 2 \times \frac{(V_{II} - V_I) \times 0,2 \times 80 \times 40}{1000}$$

$$\% \text{NaNO}_3 = 2 \times \frac{(V_{III} \times 2,5 - V_I) \times 0,2 \times 85 \times 40}{1000}$$

V_I = ml 0,2 n silver nitrate solution
 V_{II} = ml 0,2 n sodium hydroxide solution
 (Formaldehyde method)
 V_{III} = ml 0,2 n sodium hydroxide solution
 (Ion exchange method)

Molecular weights : NH_4Cl = 53,5
 NH_4NO_3 = 80
 $NaNO_3$ = 85

For example : V_I = 34,23 ml gives 29,30 % NH_4Cl
 V_{II} = 51,33 ml gives 21,89 % NH_4NO_3
 V_{III} = 29,75 ml gives 31,34 % $NaNO_3$

The described formulas are applicable only if these conditions are strictly used:

Sample weight of original explosive for extraction :
50 gram.

Normality of reagent solutions: 0,2 n.

Amount of water for dissolving the extracted residue:
1 litre.

Aliquots for argentometric and formaldehyde methods:
25 ml.

Aliquot for ion exchange analysis : 10 ml.

The accuracy of these methods is good and gives results with an error limit of 0,1 - 0,2 % absolute.

The need of time is ca. 4 hours per sample without the time for extraction and drying.

For performing the described analysis, a list of used apparatus is given below:

Laboratory equipment for wet analysis:

Electronic balance, normal glassware like pipettes, burettes, volumetric flasks, soxhlet apparatus.

Equipment for instrumental analysis:

Hitachi UV-VIS photometer U - 1100

Varian HPLC model 5060, detector UV 100,

Vista Data System 401,

Metrohm Karl-Fischer titrator type E 452 S 8 with vessel EA 875-20

Metrohm titroprocessor E 636 with silver/silver nitrate electrode.

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RAPID METHODS FOR QUANTITATION OF STABILIZERS AND THEIR REACTION PRODUCTS IN PROPELLANTS

J. BŁĄDEK
Military Technical Academy
01-489 Warsaw
Poland

M. MISZCZAK
Military Technical Armament
Institute, 05-220 Zielonka
Poland

ABSTRACT. Methods are presented for analyses of stabilizers in propellants to determine their chemical stability. The stabilizers are diphenylamine, ethylcentralite and some products of their chemical changes in single-base and double-base propellants. A large number of quantitative analyses of propellants are needed. Because of the high peak capacity of TLC methods and the relatively high viscosity of propellant sample solutions, it was decided to use HPTLC with liquid-crystalline method of visualization and densitometry. However, the liquid-crystalline method of visualization is useful for quantitative analysis of stabilizers, but is not appropriate for quantitation of many other propellants' components. The densitometric method was found to be quantitative for much more components in propellants than the liquid-crystalline one. Therefore, the densitometric method was chosen. During quantitation of stabilizers and some of their nitration products, UV absorbance signals were measured at characteristic wave lengths for analysed substances. Monotonic (increasing) standard curves describing changes of measured signals versus concentrations of analysed substances were obtained.

1. INTRODUCTION

Modern methods of propellant stability investigations are connected with quantitative instrumental analysis. In these investigations the contents of the stabilizers diphenylamine (DPA) and ethylcentralite (EC) with some of their reaction products are determined in new and stored propellants under ambient conditions and during accelerated aging. This is being done in order to recognize kinetics of propellant decomposition corresponding to stabilizer chemical changes. The basic requirement of such measurements, is the separation of components in complex propellant mixtures to isolate the stabilizer and decomposition products.

Mechanism and kinetics of DPA and EC reactions in propellants are well known [1,2]. The degree of stabilizer changes with its selected important reaction products can be a parameter of propellant chemical stability [3].

In this work, we tried to estimate the possibility of HPTLC

use for quantitative determinations of stabilizers and their products in propellants. Propellant samples selected for analysis were aged naturally (stored) under ambient conditions and heated to accelerate their decomposition and in consequence - to accelerate chemical changes of stabilizers. For quantitative measurements, liquid-crystalline method of visualization of TLC chromatograms and densitometric one were used.

2. EXPERIMENTS

2.1. Materials and Apparatus

For analytical determinations of stabilizers and some of their products, samples of single-base and double-base propellants were selected, including emulsion (ball) compositions as listed in Table 1.

TABLE 1. Characteristic compositions of propellant samples

Sample	Concentration (wt %)						
	NC	NG	DPA	EC	DNT	DBP	Others
Single-base propellant	96-99		0.7-2				0-1.8
Emulsion-free double-base propellant	56-66	20-45		0.7-3	7-12	0-5	0-1.5
Emulsion propellant	56-70	10-20	0.5-1	3-4	10-15		0-1.5

NC-nitrocellulose, NG-nitroglycerine, DNT-dinitrotoluene, DBP-dibutylphthalate, Others-technological ingredients such as camphor, graphite, etc. (Abbreviations used in Table 1 are used in the whole text).

Samples of the same lot were divided into 2 parts. One of them was heated for 1 h at 120°C in open vessel. Second one was analysed without heating. All samples were analysed to observe differences between state of chemical changes of stabilizer and its products before and after heating.

Standards: DPA, 2-nitro-DPA, 4-nitro-DPA, N-NO-DPA, EC, 4-nitro-EC, 2,4-DNT, DBP - pure for analysis (Merck), NG, NC - pure (ZTS Pronit - Poland).

Solvents: methanol, acetone, methylene chloride, hexane, ethyl acetate, benzene - pure for analysis (Merck).

Stationary phases: HPTLC plates (Merck, No: 5547, 5548, 5554).

Apparatus: CS-9000 scanning densitometer (Shimadzu), heated stage of Petrus polarization microscope (VEB Wagetechnik 'Rapido' Germany), liquid - crystalline detector (porous foil impregnated by p-pentyl-p'-cyano - biphenyl), TLC saturated chamber (Camag).

2.2. Separation of Propellant Components

Type of adsorbent, elution strength, polarity and composition of developing phase were changed, intending to isolate 'matrix' - NC or NC with

NG - in propellant solutions and to separate the rest of the components on the shortest distance of development.

A propellant sample of 0.1 g was dissolved in 10 ml of acetone or methanol. Then, 5 μ l of this solution were spotted on the start line of the HPTLC plate. Variable parameters of separations were: distance of elution, type of stationary phase and composition of mobile phase. Chromatograms were developed in a saturated chamber. In this step of analysis (optimalization of separation) chromatograms were visualized by method of fluorescence quenching. The best results of separations on TLC plates were achieved on a HPTLC 5546 plate using a ternary mixture - hexane/benzene/ethyl acetate (8:3:2) as developing phase for separation of components of double-base propellants (also in the emulsion ones), and a binary mixture of hexane and methylene chloride (7:5) for separation of components of single-base propellants. The distances of development for single-base and double-base propellants (including the emulsion ones) were 80 and 70 mm, respectively.

Values of R_F for analysed components of propellant solutions were as follows:

- single-base propellants: NC - 0, 4-nitro-DPA - 16, N-NO-DPA - 35, 2-nitro-DPA - 49, DPA - 75;
- double-base propellants (without emulsion): NC + NG - 0, 4-nitro-EC - 20, EC - 50, 2,4-DNT - 71, DBP - 86;
- emulsion propellants: NC and NG - 0, EC - 50, 2,4-DNT - 71, DPA - 92.

Chromatograms of the above propellants are presented in Figures 1-3. Analysed substances are visible in these figures as distinctly separated densitographic peaks.

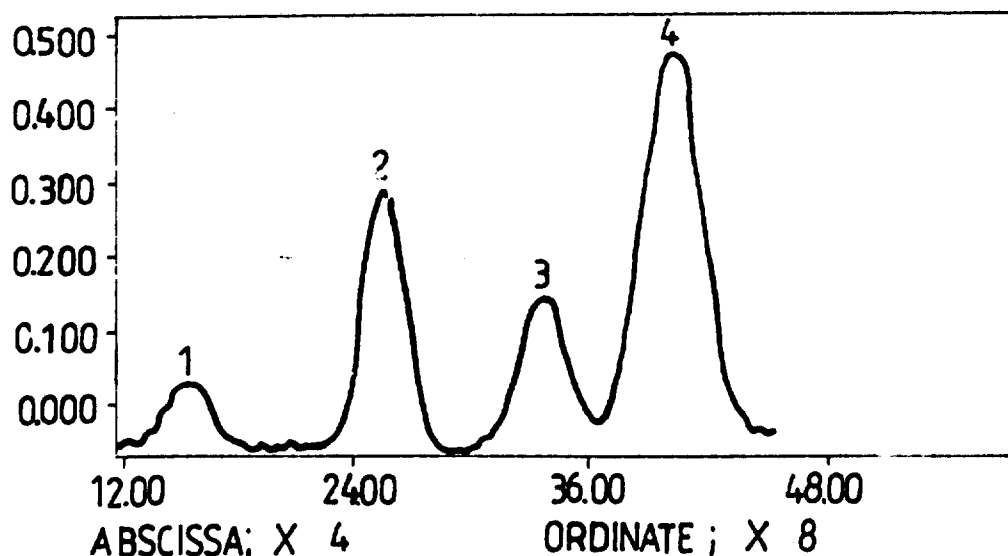


Figure 1. Densitogram of single-base propellant. Peaks point positions of spots on TLC chromatogram: 1 - 4-nitro-DPA, 2 - N-NO-DPA, 3 - 2-nitro-DPA, 4 - DPA.

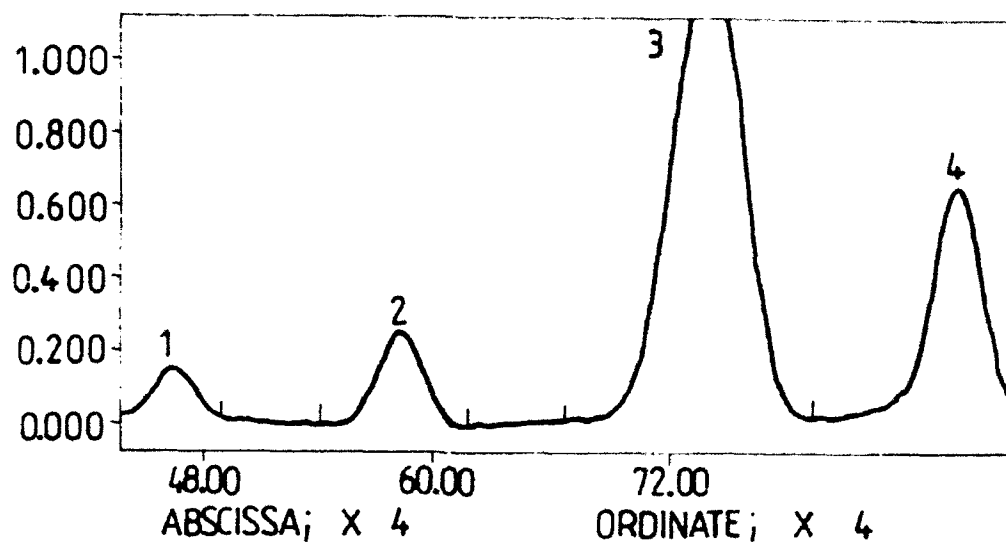


Figure 2. Densitogram of double-base propellant. Peaks point positions of spots on TLC chromatogram: 1 - 4-nitro-EC, 2 - EC, 3 - 2,4-DNT, 4 - GEP.

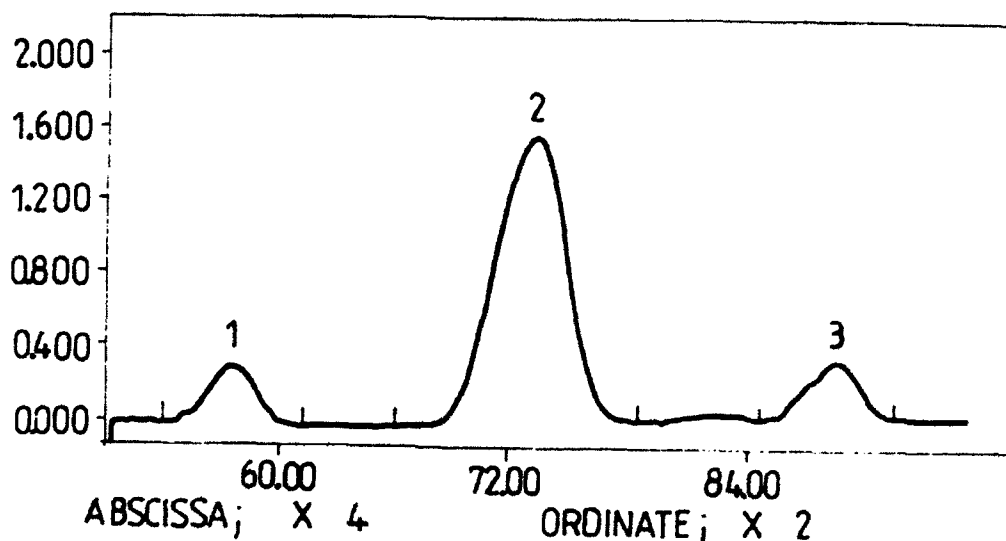


Figure 3. Densitogram of new emulsion propellant. Peaks point positions of spots on TLC chromatogram: 1 - EC, 2 - 2,4-DNT, 3 - GEP.

2.3. Quantitation of Propellants' Components

Quantitative determination of analysed substance spot 'in situ' is possible in TLC in the following cases:

- analysis of fluorescent substances (measurement of fluorescence intensity),
- combination of area measurement of spot and intensity of its colour: characteristic one or caused by chemical reaction,

- combined measurements of spot area and light absorption (transmission) at characteristic wave length, for analysed substance.

In TLC, elution methods have also been used for chromatogram visualization. The liquid-crystalline method of visualization provides the best quantitative results [4,5]. The liquid crystal method of visualizing TLC chromatograms relies on the transfer of substances separated by chromatographic system, from adsorbent to a thin film of a liquid crystal referred to as liquid crystalline detector. This is achieved by direct contact of the detector with the developed chromatogram under moderate pressure exerted by a flexible membrane. Substances to be determined dissolve in the liquid crystal and become visible in linearly polarized light by virtue of changes in the optical properties of the detector at these positions where the presence of the substance which is being analysed, causes a change in the chemical composition of the liquid-crystalline layer. In this way, a chromatogram is mapped and the spots of substances to be determined, which were invisible on the adsorbent, appear on the detector as spots whose colors differ distinctly from the background.

The best color effects are obtained using nematic liquid crystals. The detection depends on the formation (at the sites of occurrence of spots) of local binary (or more complex) systems comprising the nematic liquid crystal (mesogene) and the substance to be determined (non-mesogene) in which the liquid crystal plays the role of the solvent. It has been shown [6,7] that by simple expedient of measuring the temperature corresponding to the transition between the appearance and disappearance of spots of DPA, EC and some of their important products on the liquid crystalline detector, the method can be successful used for quantitative determinations. But, unfortunately mononitro derivatives of DPA and EC are not easily soluble in many liquid crystals, therefore in further investigations, it was focused on densitometric measurements 'in situ'.

Because, stabilizers are colorless (with the exception of some of their nitroderivatives) and are not fluorescent, it was decided to measure their absorption during quantitative analysis. Such measurements are used for quantitation when analysed substances have got characteristic absorption spectra. Presence of double bonds in molecules of DPA, EC and their reaction products allows to foresee 'a priori' the existence of absorption bands in their UV spectra. Therefore, it was necessary to find a wave length (λ_{\max}) in the UV region, at which one absorption maximum occurs. To this end, determined substances were spotted on TLC plates to approximate conditions for final quantitative measurements. Next, the spots were scanned by a UV light beam and measuring the signals of reflected light. Absorption spectra were recorded by the densitometer. Characteristic wave lengths of analysed substances were determined by the maxima of absorption peaks. As example, in Figure 4, the spectrum of DPA absorption is shown (λ_{\max} - 265 nm). Values of λ_{\max} for the rest of the propellant components were as follows: 11-NO-DPA - 282 nm, 2-nitro-DPA - 280 nm, 4-nitro-DPA - 360 nm, EC - 230 nm, 2,4-DNT, DBP - 235 nm and 4-nitro-EC - 320 nm. Measured values of λ_{\max} were used for quantitation. To this aim, after separation of standards of analysed substances, according to the above chromatographic conditions, spots of each component were scanned by a 'zig-zag' method using light wave length of λ_{\max} . Measured signals were areas (A) of densitometric peaks.

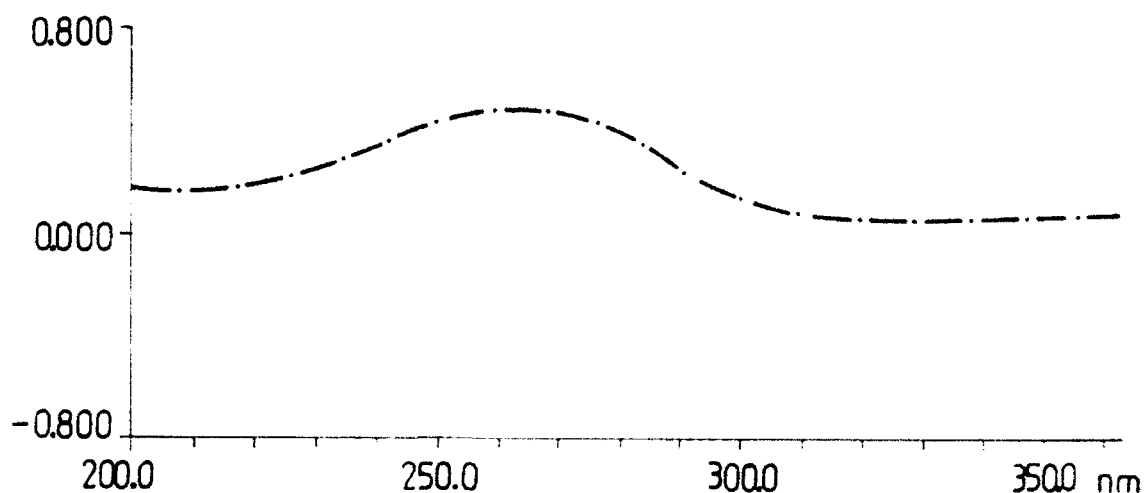


Figure 4. UV absorption spectrum of DPA.

In every case linear relation $A = f(c)$ was obtained, where (c) - concentration of analysed substance in spots. Example of such linear dependence can be the curve shown in Figure 5. Results of these measurements permitted to make standard curves for all analysed substances. Linear dependence of peaks' areas on concentrations shows the possibility of application of densitometric measurements to quantitative determinations, and in consequence to appreciate the chemical stability of propellants on the basis of stabilizer reaction dynamics.

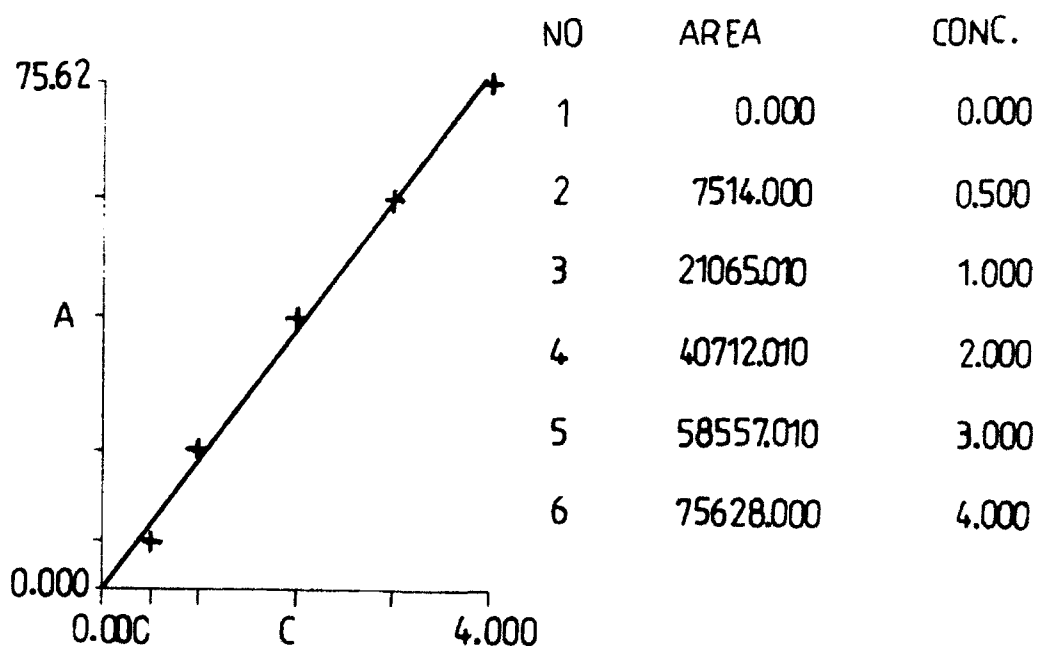


Figure 5. Standard curve of EC.

To evaluate the method's error, standard solutions of all determined substances - each one at 2 different concentrations in the range corresponding to their concentrations in propellants - were prepared. Keeping the above conditions of chromatographic separation and quantitation constant, values of concentrations for these solutions were calculated from corresponding standard curves. The number of determinations for each measuring series was 10, and there were 2 series for each of both concentrations of analysed components. Error of quantitation was in the 0.3-1.7% range. The relatively low error of these quantitations originates from simultaneous application of a relatively large volume of solution on the ILC plate - 5 μ l, and also from relatively small concentrations of determined substances in the solution (10^{-4} - 10^{-3}). Detection limit for analysed substances were in the 10^{-4} - 10^{-3} range.

Results of quantitative measurements for DPA and EC performed on selected samples at only one concentration from each measuring series by the liquid-crystalline detector were comparable with these ones obtained from densitometric measurements.

2.4. Chemical Stability Investigations

To introduce the performed quantitation method into control tests of chemical stability, 50 lots of single-base propellants and 50 lots of double-base ones comprising emulsion ones new or aged during storage under ambient conditions up to 50 years were selected.

It was expected that after propellant heating, the stabilizer content would be smaller than before heating, and in parallel the contents of reaction products should be less before heating and greater after it. The results of measurements with extracts of propellant samples did not confirm these expectations. In many cases, especially in single-base propellants, a greater content of DPA was observed after heating than before it. However, the increase in DPA reaction products contribution met the expectations. After heating NC fibres became more 'open' for extractant penetration, so the greater amounts of stabilizer could be extracted from the propellant 'grains'. Investigations with dissolved propellant samples (not extracted) confirmed this suggestion. In all dissolved samples, content of DPA was greater before than after heating. Moreover, contents of stabilizers and their reaction products in the same samples, but dissolved, (normalized to unit of propellant mass) were greater by 5-10% in comparison with their contents in extracted samples. This points that easy and effective quantitative analysis of stabilizers and their products can be performed only by means of propellant dissolving. This fact suggests the use of ILC in measurements because of relatively high viscosity of propellant solutions caused by 'matrix'.

In this method of analysis, attention was given to 'matrix' stoppage on start line of chromatogram ($hR_f = 0$) to avoid 'overloading' of the ILC plate and masking of analysed spots by 'matrix' (its streak). The chromatographic system of separation was therefore precisely selected.

Correct conditions for quantitation were chosen taking into consideration minimum signal detectable by densitometer and maximum width of scanning path. As these ones directly connected with the volume of solution applied on the start line and the concentrations of analysed substances and the viscosity of propellant solution, 5 μ l of propellant solution consisting of 0.1 g of propellant and 10 ml of solvent was chosen.

Among 100 analysed lots of propellants, some unstable ones were found in which a considerable part of the stabilizer changed into its reaction products.

In single-base propellants type 12/7, 9/7 and 7/7 (first number means thickness of burning layer in tenth of mm, second one it is number of holes in propellant 'grain') correspondingly stored for 48, 47 and 41 years, consumptions of DPA in the range 75-100% were determined. The main products of DPA chemical changes were: N-NO-DPA, 4-nitro-DPA, 2-nitro-DPA and also traces of dinitro-DPA. The degree of DPA changes in some of the lots of propellants is up to 10 times greater than that one in the majority of stable propellants of similar composition, stored during the same period under similar conditions. Mostly often observed differences in concentrations of DPA before and after heating were in the range 0.2-0.6%. In some of the propellants of type 12/7, stored for 48, 47 and 41 years, containing before heating DPA in the range 1.5-2%, 0.1-0.2% N-NO-DPA and traces of mononitro derivatives of DPA, after heating, DPA changed mainly into N-NO-DPA (in ca 90%) and into mononitro - DPA (in ca 7%). Such degree of DPA changes in some lots of unstable propellants during natural and accelerated aging points to low quality of propellant components particularly NC. Moreover, the influence of propellant component's quality on chemical stability is considerably greater than 'age' of propellant, because in most propellants of the same 'age' and the same or similar composition, dynamics of stabilizer reactions during natural and artificial aging is similar, but it can be distinctly diversified when the propellants have different quality.

In most stable double-base propellants during storage up to 50 years, a small decrease of EC content was observed in the range of 5-10% in relation to starting EC content. Rarely, traces of 4-nitro-EC were found. But surprisingly some unstable double-base gun propellants of type 16/1 and 19/1 stored for 40 and 37 years, respectively and mortar ones stored for 38, 23 and 22 years were found in which 90-100% EC changed into its reaction products - in high degree into mononitro - EC. So, the dynamics of EC chemical changes under ambient conditions in such propellants, when comparing stable ones of similar composition and the same age, is even 10 times greater. Studying chemical changes of EC in stable propellants before and after heating, differences in EC concentrations in the range 0.2-0.6% were determined. But recently, some double-base gun propellants of type 18/1 stored for 22 and 12 years, and mortar ones stored for 40, 39, 21 and 17 years were found in which all or almost all EC changed first of all into mono- and dinitro - EC. Thus, the quality of basic components of propellants has greater influence on their decomposition than their 'age'. Dynamics of DPA and EC contents decrease during storage for up to 50 years under ambient conditions is 10^4 to 10^5 less than that under the accelerated aging for 1 h at 120°C.

Results of quantitations confirm the usefulness of the analytical method based on dissolving of propellant sample, TLC separation and densitometric quantitative measurements to determine the chemical stability of propellants.

3. CONCLUSIONS

The analytical methods used to determine stabilizers and their reaction products in propellants seem to be the most suitable and reliable ones. Preparation of propellant samples by dissolving is more effective with respect to their extractions. This fact limits the use of column liquid chromatography because of high viscosity solutions. Injection of propellant solution into HPLC system, most often leads to rapid destruction of the chromatographic column. As is well known, GC is also not always suitable for such investigations because of thermal decomposition of stabilizers and their reaction products. Thus, TLC seems to be the most suitable method of propellant analysis. This method meets the principal requirements of analysis i.e. separation of sample components and quantitation with precision and reproducibility. The TLC method is characterized by the possibility to conduct many analyses during a relatively short time.

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**FLUOROMETRIC DETERMINATION OF MMAN AS A SENSITIZER IN WATER GEL
EXPLOSIVES BY HPLC USING PRE-COLUMN DERIVATIZATION WITH
7-DIMETHYLAMINOCOUMARIN-3-CARBONYL FLUORIDE**

Ken-ichi TAKA-ICHI

Identification Laboratory, National Research Institute of
Police Science
6, Sanban-cho, Chiyoda-ku, Tokyo 102, JAPAN

ABSTRACT. A new method for the determination of monomethylamine nitrate and its related aliphatic amine nitrates, used as sensitizing agent in water gel explosives, is presented.

The reaction of 7-dimethylaminocoumarin-3-carbonyl fluoride with primary or secondary amines proceeds under mild conditions and is completed in 30 seconds, even if in the presence of water. The derivatives were highly fluorescent compounds.

Ten aliphatic amine derivatives were separated in 16 minutes. A linearity range of 20 to 80 nM/mL was obtained for the calibration graph of the monomethylamine nitrate. The detection limit was under 1 picomole for an injection volume of 10 μ L.

1. INTRODUCTION

Monomethylamine nitrate(**MMAN**), 2-aminoethanol and aliphatic amine nitrates are well-known as sensitizers in water gel explosives(**WGE**).

In Japan, as well as in foreign countries, the production of the **WGE** is gradually increasing every year because it can be handled safely.

On the other hand, the production of nitroglycerin-based explosives is decreasing because it should be handled with care during the manufacturing, transportation, storage and use.

It can therefore be presumed that the **WGE** will be used for many explosion applications in the future. During the past 10 years, there was only one criminal case using **WGE** in Japan.

MMAN and its related sensitizers in the **WGE** have been studied for the determination of the scene of explosion. Thin-layer chromatographic method and chemical spot tests for the determination of **MMAN** have been reported by **R.G.Parker**(1) and **G.F.Peterson** et al(2).

Determination of low aliphatic amines in environmental, food and biological samples using gas chromatography(GC) have been reported by **K. Kuwata** et al(3).

However, with these conventional methods, it is difficult to determine many of the sensitizers having high adsorptive activity because of

strong polar groups.

Many methods for the determination of monomethylamine and the low aliphatic amine derivatives by high performance liquid chromatography (HPLC) have been developed. Dansyl derivatives, typical derivatives for the fluorometric detection method, have been reported by **R.J.Prime** and **J.Krebs(4)**. **J.Lin** and **C.Lai(5)**, using HPLC fitted with a UV detector with dansyl derivatives of primary and secondary amines have been determined in fish and shrimp samples.

However, the preparation of these UV and fluorescent derivatives is a tedious and time-consuming procedure, including extraction for the HPLC.

H.Fujino(6) and **A.Takadate(7)** showed that 7-dimethylaminocoumarin-3-carbonyl fluoride(**MACF**) was suitable as a fluorescent labeling reagent for the determination of amines and peptides. This procedure is simple, and its reagent for the amine is stable, even in the presence of water.

However, these reports were not concerned with the separation of the low aliphatic amines having two carbon atoms or less, for instance, monomethylamine and ethylamine. Separation of the low aliphatic amines was considered to be a difficult problem.

In this paper, HPLC with fluorescence detection has been developed as a method for the determination of the **MMAN** sensitizer and other additives in **WGE** with **MACF**, a fluorescence labeling reagent for the amines.

2. EXPERIMENTAL

2.1. Apparatus

The HPLC consisted of a Radial-pak C_{18} (10 $\mu m\phi$) reverse-phase column(10 cm x 8 mm I.D.) mounted in a **Waters** liquid chromatograph equipped with a Model M600 solvent delivery system, a Model U6K universal injector, a Model 990J photodiode array(**PDA**) detector, a Model 740 integrator(all products of **Waters Associates**, MA, USA), a Model **Hitachi** F-1000 fluorescence spectrophotometer(flow cell, 12 μL)(Tokyo, Japan) and a Model **Shimadzu** U-225M analog chart recorder(Kyoto, Japan).

2.2. Reagents

2.2.1. Aliphatic amines and chemicals. **MMAN** was synthesized by reacting monomethylamine with nitric acid. All of the aliphatic amines and its related compounds(sensitizer and additives) in **WGE** were purchased from **Wako Pure Chemical Industries Ltd**(Osaka, Japan).

All chemicals were of reagent grade. Both methanol and acetonitrile were of HPLC grade and were purchased from the **Wako**. The water used was distilled and deionized.

2.2.2. Buffer solutions. **McIlvaine's** buffer solution was prepared from citric acid solution(0.1 M) adjusted with disodium hydrogen phosphate solution(0.2 M) to pH 6.0. This solution was diluted ten times with water for the HPLC.

2.2.3. Syntheses of the MACF and 3-N-alkyl, 7-dimethylaminocoumarin-carboxamides. A part of the **MACF** and its precursor were presented by courtesy of Dr. H. Fujino. A large portion of the **MACF** and its related compounds were prepared according to the method of A. Takadate et al(7).

These compounds were characterized as follows: Melting points were determined on a Yanagimoto MP-S3 micro melting point apparatus (Kyoto, Japan), differential thermal analyzer and are uncorrected.

Fluorescence measurements were obtained with a Hitachi F-4500 (Tokyo, Japan) in MeOH or CH₃CN solvent. IR spectra were recorded on a Perkin-Elmer FT/IR 7700 (CO, USA).

Proton NMR (¹H-NMR) spectra were recorded on a Varian FT/NMR VXR-300S (CA, USA) with tetramethylsilane as internal standard (δ value, ppm).

The abbreviations used are as follows. s: singlet, d: doublet, dd: double doublet, t: triplet, quart: quartet, quint: quintet, hexa: hexaet

Mass spectra (MS) were measured with a Shimadzu GC/MS QP-1000 (Kyoto, Japan).

7-Dimethylaminocoumarin-3-ethylcarboxylate(I)

A mixture of 2-oxy, 4-dimethylamino-benzaldehyde and diethyl malonate in ab. EtOH was refluxed in the presence of piperidine for 3 hours.

Yellow needles, mp 166°C, Ex: 409 nm, Em: 460 nm, IR (KBr) cm⁻¹: 1622, 1519, 1747, 1200, EI/MS m/z (%): 261 (M⁺, 100), 88 (12), 189 (41), 161 (34), 132 (30), 108 (28), 107 (23), 204 (20)

7-Dimethylaminocoumarin-3-carboxylic acid(II)

A mixture of (I) and 9N-HCl solution was stirred for 30 hours at room temperature.

Yellow needles, mp 277°C, Ex: 380 nm, Em: 451 nm, IR (KBr) cm⁻¹: 1585, 1515, 1619, 1385, 1726, ¹H-NMR (CDCl₃, 300 MHz) δ: 3.18 (6H, s, -N(CH₃)₂), 6.54 (1H, d, C₈-H), 6.74 (1H, d-d, C₆-H), 7.49 (1H, d, C₅-H), 8.70 (1H, s, C₄-H), EI/MS m/z (%): 233 (M⁺, 100), 161 (69), 160 (59), 188 (38), 204 (25), 42 (25), 89 (23), 184 (20)

7-Dimethylaminocoumarin-3-carbonyl fluoride(III)

A mixture of (II) and cyanuric fluoride in CH₂Cl₂ was stirred in the presence of pyridine for 1 hour at room temperature.

Yellow needles, mp 231°C, Ex: 415 nm, Em: 463 nm (acetonitrile), IR (KBr) cm⁻¹: 1626, 1519, 1592, 1736, 1402, ¹H-NMR (CDCl₃, 300 MHz) δ: 3.17 (6H, s, -N(CH₃)₂), 6.47 (1H, d, C₈-H), 6.68 (1H, d-d, C₆-H), 7.41 (1H, d, C₅-H), 8.45 (1H, s, C₄-H), EI/MS m/z (%): 235 (M⁺, 100), 234 (66), 206 (52), 44 (30), 233 (27), 207 (24), 42 (21), 89 (17)

3-N-Alkyl, 7-dimethylaminocoumarin-carboxamides

A mixture of (III) and each of alkylamine nitrates or hydrochlorides in CH₃CN was stirred in the presence of 4-dimethylaminopyridine (DMAP) or pyridine as reaction accelerator for 1 hour at room temperature.

Each one of the yellow carboxamides was characterized as follows:

a) Carboxamide(-CONH₂)

mp 303°C, Ex: 405 nm, Em: 461 nm, IR (KBr) cm⁻¹: 1631, 1693, 1656, 1524

, 1385, $^1\text{H-NMR}(\text{CDCl}_3, 300 \text{ MHz})$ δ : 3.13(6H, s, $-\text{N}(\text{CH}_3)_2$), 6.51(1H, d, $\text{C}_8\text{-H}$), 6.68(1H, d-d, $\text{C}_6\text{-H}$), 7.45(1H, d, $\text{C}_5\text{-H}$), 8.74(1H, s, $\text{C}_4\text{-H}$), EI/MS $m/z(\%)$: 232(M^+ , 100), 44(59), 216(40), 203(28), 204(24), 132(14), 42(13), 89(12)

b) **N-Methyl carboxamide**($-\text{CONHCH}_3$)

mp 270°C , Ex: 408 nm, Em: 466 nm, IR(KBr) cm^{-1} : 1625, 1703, 1597, 1374, 811, $^1\text{H-NMR}(\text{CDCl}_3, 300 \text{ MHz})$ δ : 3.14(6H, s, $-\text{N}(\text{CH}_3)_2$), 6.53(1H, d, $\text{C}_8\text{-H}$), 6.66(1H, d-d, $\text{C}_6\text{-H}$), 7.45(1H, d, $\text{C}_5\text{-H}$), 8.74(1H, s, $\text{C}_4\text{-H}$), EI/MS $m/z(\%)$: 216(100), 246(M^+ , 52), 59(51), 55(35), 58(31), 57(25), 72(30), 132(26)

c) **N-Ethyl carboxamide**($-\text{CONHC}_2\text{H}_5$)

mp 180°C , Ex: 404 nm, Em: 466 nm, IR(KBr) cm^{-1} : 1517, 1619, 1693, 1585, 1641, $^1\text{H-NMR}(\text{CDCl}_3, 300 \text{ MHz})$ δ : 1.28(3H, t, $-\text{CH}_3$), 3.13(6H, s, $-\text{N}(\text{CH}_3)_2$), 3.46(2H, quint, $-\text{CH}_2-$), 6.51(1H, d, $\text{C}_8\text{-H}$), 6.68(1H, d-d, $\text{C}_6\text{-H}$), 7.46(1H, d, $\text{C}_5\text{-H}$), 8.77(1H, s, $\text{C}_4\text{-H}$), EI/MS $m/z(\%)$: 44(100), 216(98), 260(M^+ , 61), 108(29), 217(28), 189(27), 161(25), 132(24)

d) **N-Propyl carboxamide**($-\text{CONHC}_3\text{H}_7$)

mp 154°C , Ex: 406 nm, Em: 465 nm, IR(KBr) cm^{-1} : 1519, 1619, 1698, 1586, 1392, $^1\text{H-NMR}(\text{CDCl}_3, 300 \text{ MHz})$ δ : 0.99(3H, t, $-\text{CH}_3$), 1.64(2H, hexa, $-\text{CH}_2-$), 3.13(6H, s, $-\text{N}(\text{CH}_3)_2$), 3.45(2H, quart, $-\text{CH}_2-$), 6.51(1H, d, $\text{C}_8\text{-H}$), 6.68(1H, d-d, $\text{C}_6\text{-H}$), 7.46(1H, d, $\text{C}_5\text{-H}$), 8.74(1H, s, $\text{C}_4\text{-H}$), EI/MS $m/z(\%)$: 216(100), 232(34), 58(30), 274(M^+ , 29), 108(21), 217(18), 132(17), 189(9)

e) **N-Butyl carboxamide**($-\text{CONHC}_4\text{H}_9$)

mp 133°C , Ex: 401 nm, Em: 461 nm, IR(KBr) cm^{-1} : 1515, 1689, 1619, 1580, 1396, $^1\text{H-NMR}(\text{CDCl}_3, 300 \text{ MHz})$ δ : 0.95(3H, t, $-\text{CH}_3$), 1.42(2H, hexa, $-\text{CH}_2-$), 1.61(2H, quint, $-\text{CH}_2-$), 3.12(6H, s, $-\text{N}(\text{CH}_3)_2$), 3.45(2H, quart, $-\text{CH}_2-$), 6.51(1H, d, $\text{C}_8\text{-H}$), 6.67(1H, d-d, $\text{C}_6\text{-H}$), 7.45(1H, d, $\text{C}_5\text{-H}$), 8.73(1H, s, $\text{C}_4\text{-H}$), EI/MS $m/z(\%)$: 216(100), 232(32), 288(M^+ , 28), 217(19), 72(19), 132(17), 108(14), 246(11), 233(9)

2.3. Sample Preparation for the HPLC

7-Dimethylaminocoumarin-3-carboxamide derivatives of aliphatic amines in the WGE (Table 1) were prepared by reacting 20 μL of 0.5 mM **MACF**- CH_3CN solution with each 20 μL of 0.05 mM amine HCl or HNO_3 salt- CH_3CN solution, 10 μL of 0.05 mM n-butylamine HCl (internal standard)- CH_3CN solution, 20 μL of 75 mM **DMAP**- CH_3CN solution as reaction accelerator and 30 μL of CH_3CN .

The mixture was vortex-mixed thoroughly using a Model MH-10 mixer (Iuchi, Tokyo, Japan) and allowed to stand at ambient temperature for 30 seconds. A 10 μL of the clear yellow reaction mixture was taken for the HPLC analysis.

2.4. HPLC Separation and Quantitation

The separation was carried out by isocratic elution. The eluents were methanol-water (70:30, 80:20). A flow rate of 1.0 mL/min was used. The compositions of the solvent system are shown in the Table 2.

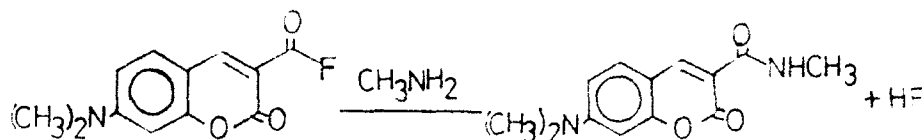
The fluorescence intensities were measured at 470 nm with excitation at 420 nm using a fluorescence spectrophotometer fitted with an integrator and an analogue recorder. At the same time, UV absorbance were monitored at 254, 390, 420 and 430 nm using a PDA detector.

The **MMAN** was quantified by the peak area ratio to the *n*-butylamine by use of an integrator.

3. RESULTS AND DISCUSSION

3.1. Derivatization of the Amines

The reaction of **MACF** with **MMAN** proceeds as follows:



MACF has been developed as a fluorescent derivatizing reagent of primary and secondary amines by HPLC. Generally speaking, when exposed to UV light, coumarin compounds fluoresces a blue color.

Moreover, 3-*N*-alkyl, 7-dimethylaminocoumarin-carbonyl compounds are highly fluorescent compounds because they have a carboxyl group at C₃-position as electron acceptor and have a dimethylamino group at C₇-position as electron donor.

Furthermore, the 7-dimethylamino derivative of the acyl fluoride is stable to water compared with 7-methoxy homologue.

3.1.1. Effect of the reaction time on the reaction. Time courses of the reaction of **MMAN** with **MACF** were investigated at various times at room temperature. As the reaction time increased, fluorescent intensity of the derivative did not increase (**Fig. 1**).

Shortening of the analysis time is important, therefore a time of 30 seconds was used for the reaction time.

3.1.2. Effect of water content on the reaction. The reaction of **MMAN** with **MACF** were investigated in varying concentrations of the reaction mixtures at room temperature.

As the water concentration increased, the fluorescence intensity decreased (**Fig. 2**). In addition, the reaction mixture changed gradually from a yellow color to colorless when in the presence of an excess of water.

However, the reaction mixture kept its yellow color for a long time in the absence of water. A reaction mixture containing less than 30% water did not affect the quantitative analysis of the derivative.

3.1.3. Effect of reaction accelerator on the reaction. The reaction of **MMAN** with **MACF** was investigated in various tertiary amines, for example, **DMAF**, triethylamine.

When **DMAP** was employed, the chromatogram gave a high response of fluorescent intensity without interfering peaks.

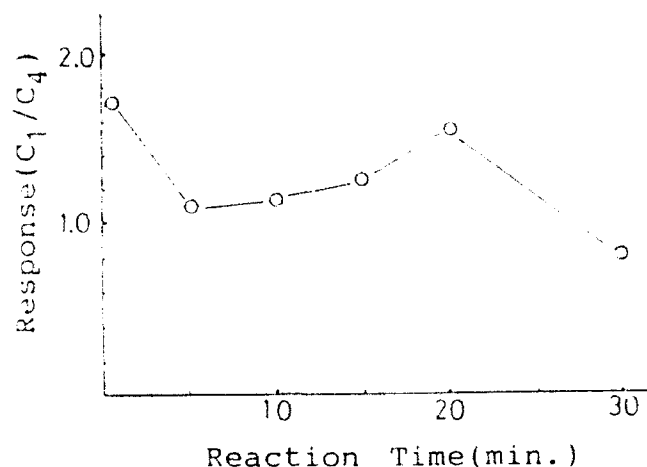


Figure 1. Effect of the reaction time on the reaction. Sample volume :10 μ L. Acetonitrile was used for sample preparation. Reaction compositions are as follows. 20 μ L of 0.01 mM **MMAN**, 30 μ L of 0.01 mM C_4 -carboxamide as internal standard, 20 μ L of 15 mM **DMAP**, 10 μ L of 1 mM **MACF** and 20 μ L of CH_3CN .

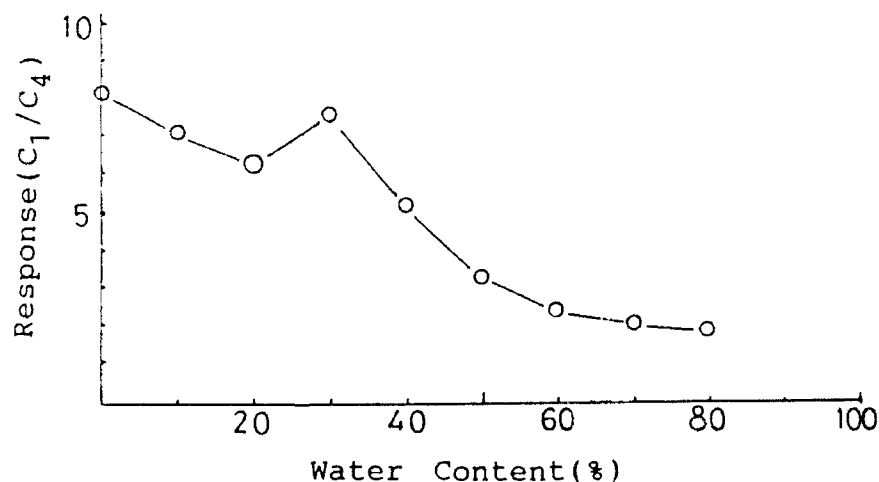


Figure 2. Effect of water content on the reaction. Sample volume and its compositions are the same as in **Fig. 1**.

Because **DMAP** is solid, it can easily be obtained as a pure reagent, to prepare the reaction mixture.

Triethylamine, pyridine and its related compounds(4-methyl;2,4-dimethyl;2,4,6-trimethyl homologues) interfered with the HPLC separation because of impurities.

3.1.4. Effect of pH and solvent on the reaction. The reaction of **MMAN** with **MACF** were investigated at various pH values and solvents at room temperature.

The results indicated that fluorescent intensity decreased when buffer solution was employed. Therefore, buffer solution was not used for the reaction mixture, as well as for HPLC analysis because the ODS (C_{18}) column was not stable in the presence of an alkaline eluent. Acetonitrile was used for the reaction.

However, when acetonitrile was used as eluent with a large excess of **DMAP**, interfering peaks due to the degradation product of the column appeared.

Methanol was not employed for the reaction because it generally contained water. However, methanol was employed for the HPLC separation because it was a cheaper eluent, and its suitability for the ODS column.

3.1.5. Effect of **MACF** concentration on the reaction. The reaction of **MMAN** with **MACF** was investigated in varying concentration of the **MACF**-acetonitrile solution at room temperature.

As the concentration of **MACF** increased, the fluorescent intensity of the derivative increased (Fig. 3). As a result, the concentration of **MACF** to **MMAN** ratio was employed over a concentration range of 10 to 50.

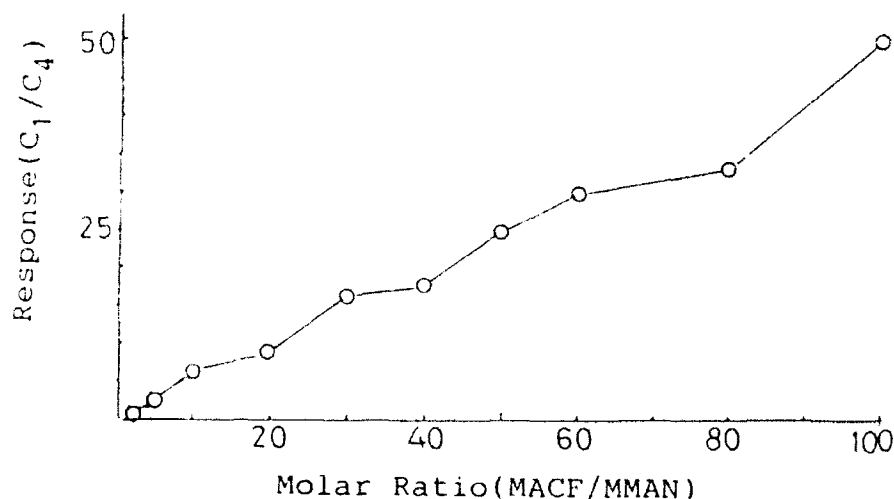


Figure 3. Effect of **MACF** concentration on the reaction. Sample compositions are as follows. 20 μ L of 0.01 mM **MMAN**, 20 μ L of 0.01 mM C_4 -carboxamide as internal standard, 20 μ L of 15 mM **DMAP**, 20 μ L of CH_3CN , 20 μ L of various concentrations of the **MACF**.

3.1.6. Effect of **DMAP** concentration on the reaction. The reaction of **MMAN** with **MACF** was investigated in varying concentration of the **DMAP**-acetonitrile solution at room temperature.

As the concentration of **DMAP** increased, fluorescent intensity of the derivative increased (Fig. 4).

When the concentration of **DMAP** to **MMAN** ratio was 50, the derivative gave a high response of the fluorescent intensity.

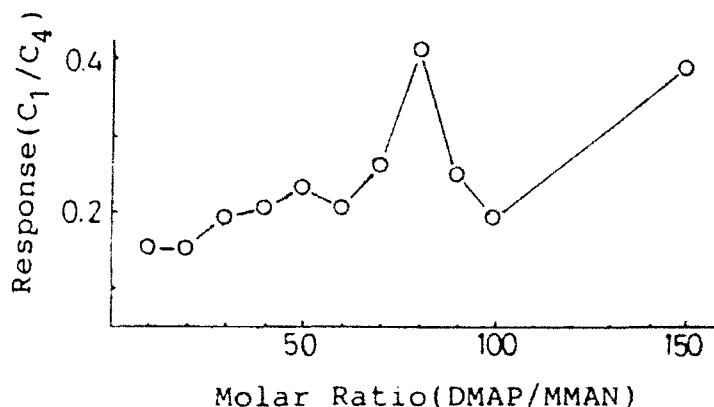


Figure 4. Effect of **DMAP** concentration on the reaction. Sample volume: 10 μ L. Reaction compositions are as follow: 20 μ L of 0.01 mM **MMAN**, 20 μ L of 0.01 mM **C₄-carboxamide**, 20 μ L of 0.5 mM **MACF**, 20 μ L of **CH₃CN** and 20 μ L of various concentrations of **DMAP**.

However, a large excess of **DMAP** affected the peak shape and peak sensitivity of the carboxamate derivatives because the reaction mixture was a strong base.

When **DMAP** was not used for the reaction as reaction accelerator, the peak of the derivative was not found. And the peak of **MACF** appeared in the vicinity of the **MMAN** derivative.

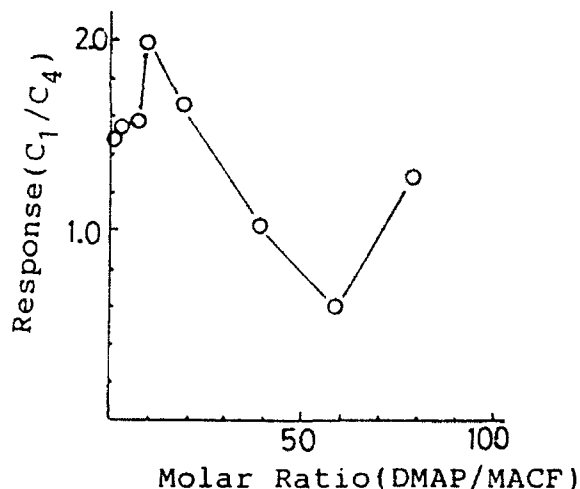


Figure 5. Effect of **DMAP** to **MACF** concentration ratio. Sample volume: 10 μ L. Sample compositions: 20 μ L of 0.01 mM **MMAN**, 20 μ L of 0.005 mM **C₄-carboxamide** (internal standard), 20 μ L of 0.5 mM **MACF**, 20 μ L of **CH₃CN** and various concentration of **DMAP**.

Similarly, the effect of **DMAP** to **MACF** concentration ratio on the

reaction was investigated at the same time. When a **DMAP** to **MMAN** ratio of 10 was used, the derivative gave a high response of the fluorescent intensity(**Fig. 5**).

The water, **MACF** and **DMAP** content in the reaction mixture were important factors in the preparation of the derivatives.

3.2. HPLC Separation of Carboxamide Derivatives

Figure 6 shows the separation by HPLC isocratic elution of 5 aliphatic amines in a standard solution. The separation took less than 16 minutes. A summary of the retention times and electronic absorption maxima of the carboxamides derived from 17 aliphatic amines are given in **Table 1**.

The peak of ammonium derived from ammonium nitrate was found to be small, but it was found ordinarily in the presence of a high concentration of ammonium ion.

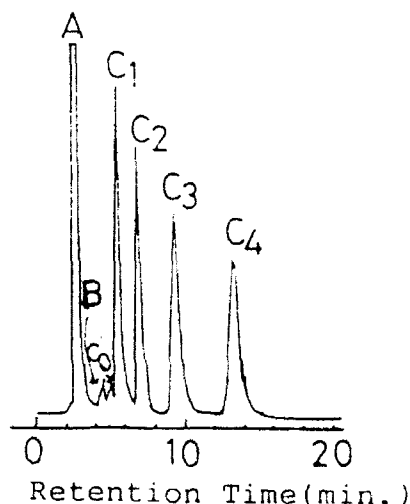


Figure 6. HPLC separation of five aliphatic amine standards, derivatized by the reaction with the **MACF**. A:hydrolysate, impurity of the **MACF**, and by-product peak due to the reaction. B:**MACF** $C_0:NH_4NO_3$ $C_1:CH_3NH_2$ $C_2:C_2H_5NH_2$ $C_3:n-C_3H_7NH_2$ $C_4:n-C_4H_9NH_2$ Sample volume:10 μ L Column: Radial pak C_{18} Standard:40 ng for each except C_0 (80ng) Mobile phase: MeOH/ H_2O (70/30) Flow rate:1.0 mL/min Sensitivity:0.1

The typical electronic spectra of the carboxamides of 4 amines and carboxylic derivative are illustrated in **Figure 7**.

3.2.1. The selection of fluorescence wavelength. As mentioned above, the maximal exciting and emission wavelength of fluorescent spectra of the **MMAN** derivative using 100 % methanol were 408 and 466 nm, respectively. In case of this HPLC method, maximal UV absorption spectrum of the **MMAN** derivative was 419 nm.

In case of 100 % methanol solvent, maximal UV absorption spectra of the carboxamides were shifted to slightly lower wavelengths(412 nm).

TABLE 1. Retention times(min.) and electronic absorption peaks(nm) of 3-N-alkyl, 7-dimethylaminocoumarin-carboxamides

Amine	Rt(min.)	R.R.T	UVmax(nm)
1.Ammonium nitrate	4.6	0.49	420
2.Monomethylamine	5.5	0.59	419
3.Ethylamine	7.0	0.74	420
4.n-Propylamine	9.4	1.00	420
5.n-Butylamine	13.4	1.43	420
6.Ethylenediamine	9.4	1.00	421
7.2-Aminoethanol	4.1	0.44	420
8.Hydrazine	4.5	0.48	420
9.Trimethylamine	----	----	---
10.Urea	----	----	---
11.Aniline	----	----	---
12.Ethyleneglycol	----	----	---
13.Propyleneglycol	----	----	---
14.Dimethylamine	4.0	0.43	402
15.Aminoacetonitrile	4.3	0.45	424
16.Thiourea	----	----	---
17.Formamide	----	----	---
18.MAC-COOH	2.3	0.24	394
19.MACF	4.3	0.46	430

No.1-13....Sensitizers and its related compounds in WGE except No.5

No.14-17...Additives in WGE

No.18.....Hydrolysis product and impurity of the MACF (7-Dimethylaminocoumarin-3-carboxylic acid)

No.19.....Fluorescent derivatizing agent

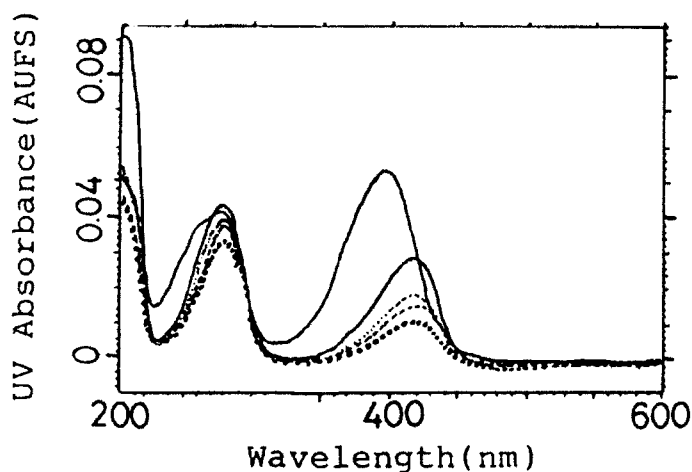


Figure 7. Electronic absorption spectra of 3-N-alkyl, 7-dimethylaminocoumarin-carboxamides. The UV spectra from the top to the bottom are

carboxylic acid, monomethylamine, ethylamine, n-propylamine and n-butylamine, respectively. These UV spectra corresponding to the **Figure 6** were measured simultaneously by a **PDA** detector.

Therefore, the fluorescence intensities were measured at 470 nm with excitation at 420 nm.

3.2.2. Separation by HPLC. The methanol, ethanol, acetonitrile, water and its buffer solution were studied as mobile phases. As a result, methanol-water solutions(70:30, 80:20) were used(**Table 2**).

TABLE 2. HPLC data of 3-N-alkyl, 7-dimethylamino-coumarin-carboxamides

Retention time(min.)					
Solvent system	Ammonium nitrate	Methyl amine	Ethyl amine	n-Propyl amine	n-Butyl amine
1	8.3	9.3	10.3	12.0	14.4
2	4.0	4.6	5.4	6.5	8.0
3	7.6	8.7	10.0	12.0	15.2
4	3.8	4.4	5.0	6.0	7.4
5	9.2	11.6	15.2	21.8	34.0
6	4.6	5.5	7.0	9.4	13.4

Solvent systems

1:MeOH/citric acid buffer(pH6.0)(80:20)	flow rate 0.5 mL/min
2:MeOH/0.1%AcOH-H ₂ O(pH3.3)(80:20)	flow rate 0.5 mL/min
3:MeOH/H ₂ O (80:20)	flow rate 0.5 mL/min
4:MeOH/H ₂ O (80:20)	flow rate 1.0 mL/min
5:MeOH/H ₂ O (70:30)	flow rate 0.5 mL/min
6:MeOH/H ₂ O (70:30)	flow rate 1.0 mL/min

Buffer solutions were not used for this method, because the pH value of the eluent was 7.3. When less than 60 % methanol-water elution was used, analysis time took longer to separate the amine derivatives.

A broad peak appeared as background when an acetonitrile-water solution was used as mobile phase with an excess of **DMAP**. The peak area derived from **MACF** increased in proportion to the amount of **MACF**.

However, those peaks decreased in inverse proportion to the amount of amine. The peaks derived from excess of **MACF** appeared in the vicinity of the peak of the **MMAN** derivatives(**Fig. 8**). Those peaks gave a slight interference with quantitative analysis of **MMAN**. This problem has been solved by using a **PDA** detector, monitoring at 430 nm for **MACF**, and at 420 nm for the **MMAN** derivative.

The peak of 7-dimethylaminocoumarin-3-carboxylic acid, derived from hydrolysis product in the presence of an excess of water or impurity of **MACF**, appeared as a big peak. This peak does not interfere with the quantitative and qualitative analyses of **MMAN**.

But, it was not a problem because of the monitoring at 390 nm. In

general, a water content less than 30 % in the reaction mixture did not interfere with the quantitation.

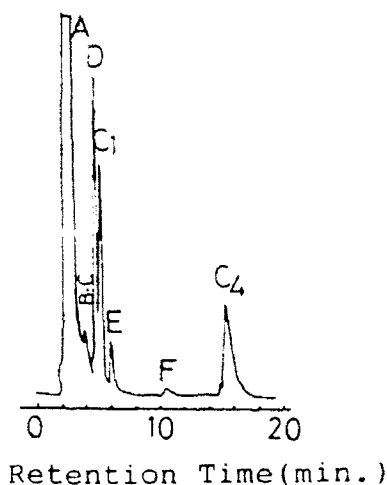


Figure 8. HPLC separation in the case of low concentration of mono-methylamine for the calibration graph, or in the case of a large excess of **MACF**. C_1 : CH_3NH_2 (60 nM/mL) C_4 : $n\text{-C}_4\text{H}_9\text{NH}_2$ (internal standard, 50 nM/mL). A: Carboxylic derivative (hydrolysate or impurity of **MACF** (500 nM/mL). B, C, E and F: These peaks are due to the reaction mixture. D: **MACF**. Column: Radial Pak C_{18} Mobile phase: $\text{MeOH}/\text{H}_2\text{O}$ (70/30) Flow rate: 1.0 mL/min Sample volume: 10 μL Sensitivity: 1.0

The peaks of urea, formamide, aniline, thiourea, ethyleneglycol, propyleneglycol and trimethylamine were not found in this method.

3.3. Calibration of **MMAN**

Figure 9 shows the result of the calibration graph of **MMAN**. The response curve for injection ranging from 20 to 80 nM/mL was linear. But, when using a peak height ratio, the calibration graph did not show linearity.

However, at high concentration of **MMAN** (ranging from 0.25 to 4 $\mu\text{M}/\text{mL}$) and water content less than 30 % in the reaction mixture good linearity was obtained using *n*-propylamine as internal standard. In this case, both peak area and peak height ratio could be used for the calibration graph using the PDA detector (at 420 nm) and an analogue chart recorder (sensitivity, 0.1).

It was considered that peak D (**MACF**), and F, derived from **MACF**, shown in Figure 8, did not interfere with the calibration graph.

3.4. Detection Limit

The lower limit of detection of **MMAN** was under 1 pico-mole for an injection of 10 μL .

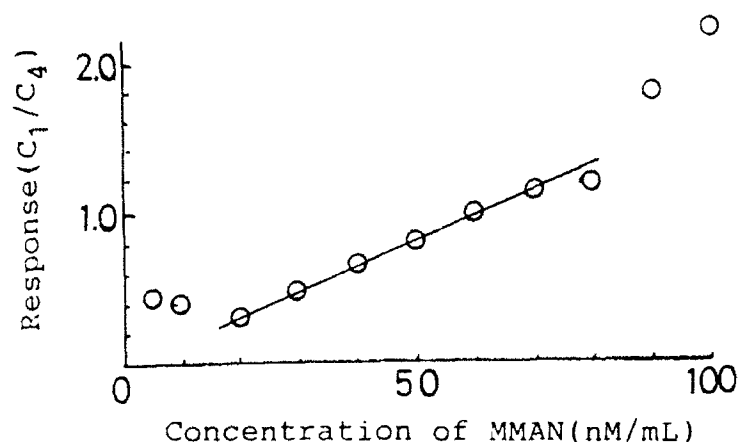


Figure 9. Calibration graph for the **MMAN**

3.5. Comparison with Other Methods

Procedure for the sample preparation of the carboxamide derivative was very simple in comparison with dansyl-, dabsyl- and 2,4-dinitrophenylamine derivatives(8) for HPLC. This because it was not necessary to heat the reaction mixture for a long time for the derivatization of amine and extraction of the analyte from the reaction mixture.

However, preparation of dansyl- and dabsylamine derivatives of **MMAN** are complicated to derivatize, and dansylamine derivatives for fluorescent detection are not stable.

Although, the dabsylamine derivatives are stable, sensitivity of the UV detection method is not so high as that of fluorometric detection.

D.J.Reutter(9) and **D.J.Barsotti(10)** have reported on **MMAN** using ion chromatography(IC). With the IC method, it is difficult to separate methylamine containing a large quantity of ammonium ion, because the peak of the ammonium ion appears in the vicinity of the peak of the methylamine.

4. CONCLUSION

Monomethylamine nitrate as sensitizer was separated and determined by HPLC using a fluorescent derivative with 7-dimethylaminocoumarin-3-carbonyl fluoride. The derivative of the amine could be prepared easily within 30 seconds and was stable even if the reaction mixture contained water. In the same manner, its related amine derivatives, including 2-aminoethanol were determined within 16 min.

It was concluded that the **MACF** derivatives for the determination of **MMAN** was good for fluorescent labeling reagent. Similarly, this method may be applicable to forensic compounds having primary and secondary

aliphatic amino groups.

5. ACKNOWLEDGMENT

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Analysis of the Detonation Products of Insensitive High Explosives

F. Volk

Fraunhofer-Institut für Chemische Technologie (ICT)

7507 Pfinztal, D

Abstract

The detonation products of high explosives are dependent on pressure and also on the confinement under which the detonation reaction proceeds. To determine the detonation products of less sensitive high explosives such as TNT/nitroguanidine (NQ) and PBX charges with polybutadiene (PB) binder containing RDX together with or without aluminium (Al) experiments have been performed in a stainless steel chamber of a volume of 1.5 m³. These experiments were done under different ambient argon pressures up to 0.3 MPa. Gaseous reaction products were analysed by mass spectrometry and chemiluminescence analysis. Solid reaction products were analysed for measuring the carbon residue or unreacted Al.

It was found that the detonation products were highly dependent on the ambient pressure of argon. The most important changes of the reaction products and therefore also of the energy output were found between vacuum and atmospheric pressure of argon. With increasing pressure, H₂ and CO decrease and CO₂, H₂, C_s, NH₃ and CH₄ increase together with the reaction enthalpy. By analysing the physical structure of the carbon residue, diamonds have been observed between 4 and 7 nm diameter.

1. Introduction

Some years ago, safety programs have been started with the aim of developing so-called insensitive high explosives (IHE). These explosives should be safe as far as possible against heat, radiation, external fire, impact, friction and shocks. The explosive charges are composed of insensitive explosive components such as TATB, Nitroguanidine, NTO, etc. But also compositions with plastic bonded explosive components exhibit properties of insensitive or less sensitive high explosives.

The energy output released during the detonation reaction of explosives depends on the following parameters:

- energy of the charge,
- oxygen balance,
- grain size of the components,
- degree of confinement and
- completeness of the reaction of metals, such as Al, with the reaction products of the explosive.

Confinement influences reaction in so far as it adds resistance to the expansion of the gaseous detonation products and maintains high pressures and temperatures for a longer period of time before lateral rarefactions quench reaction.¹⁾

By using a confinement, the Boudouard-Equilibrium



is influenced to form higher concentrations of CO_2 and C_s . Additionally, the amount of H_2O increases whereas H_2 and CO decrease²⁾. Both reactions increase the heat of detonation of confined charges.

Earlier investigations have shown that less sensitive high explosives consisting of TNT and nitroguanidine produced very different detonation products when initiated in vacuum compared with those under one atmosphere of argon ³⁾. It is assumed that argon behaves as a confining medium, because the reshocking of the reaction products is reduced dramatically when going from vacuum to 0,1 MPa of argon.

In order to learn more about prepressurization, other high explosives such as plastic bonded (PBX) charges based on RDX and nitroguanidine with and without additional aluminium in a stainless steel containment were studied. By varying the argon pressure from vacuum up to 0,3 MPa, the detonation products were analyzed with regard to the gas and the soot formation. Additionally the heat output was evaluated.

2. Experiments

For the experiments a stainless steel containment with a volume of 1,5 m³ was used.

The cylindrical high explosive charges had a mass of about 300 g without booster. For the initiation, a detonator cap No 8 together with a 10 g RDX booster were used. Because of the corner effect a second booster of about 18 g having the same diameter as the main charge was glued onto the charge ⁴⁾. After hanging the explosive horizontally inside the containment, the vacuum pump was started in order to provide a detonation in vacuum or at different pressures of argon. For the reduced pressure experiments we used a vacuum pump which produced after 15 minutes a pressure of about 2 mm Hg.

After firing, gas samples were taken for the measurement of the NO content in a NO_x-Analyzer and the mass spectrometric analysis of the gas products. The reproducibility of the gas composition of several shots was about $\pm 0,5$ mol% relative to the mean value.

After the shot the containment was opened and the solid residue collected. This was analyzed for carbon, hydrogen and nitrogen as well as for unreacted aluminium by measuring the H₂ formation after treating with HCl.

The solid residue was dried in order to be able to analyze it completely for C, H, N and unreacted Al. For qualifying the analysis, in all cases the theoretical mass balance was calculated and compared with the experimental balance ratio of N/C; N/H and N/O.

Because detonator caps consisting of copper sleeves were used, there was no contamination of the unreacted Al contained in the soot.

In some cases, the soot was examined in more detail at the Los Alamos National Laboratory by using X-ray diffraction and convergent-beam electron diffraction. Previous investigations have shown that X-ray diffraction powder patterns exhibit the same diamond spacings as an authentic diamond sample.⁵⁾

The following explosive charges have been investigated:

- Charges of TNT und spherical Nitroguanidine (NQ) with a grain size distribution of the NQ spherules of 28 % with 150 - 200 μm and 72 % with 500 - 1000 μm ,
- Charges with Polybutadiene (PB) binder (PBX) and
- PBX charges containing aluminium (Al)

The density and detonation velocity of the explosive charges was as follows in Table 1:

Composition	Density g/cm ³	Detonation Velocity m/s
TNT	1,64	6 900
45 % TNT/55 % NQ	1,63	7 724
45 % TNT/55 % NQ (Glass Confinement)	1,63	7 724
HX 72:		
80 % RDX (10 μm)/20%PB	1,48	7 750
HX 76:		
HXA 123:		
56% RDX class C/14% RDX(10 μm) 1,62		7 350
15% PB/15 % Al Alcan 400		

The detonation velocity was measured using explosive charges with 40 mm in diameter and 350 mm in length. The charges were confined in hardpaper tubes with wall thickness of 1,5 mm. Ionization pins were used for the velocity measurements.

The critical diameter of NQ containing charges was about 20 to 25 mm. Because charge diameters of 50 mm and charge lengths of more than 90 mm were used, complete detonation reaction must have been achieved.

3. Results

3.1 Reaction Products of TNT

The reaction products of a charge consisting of 300 g TNT and 29 g booster without confinement were compared with those published by D.Ornellas ²⁾, found using detonation calorimetry, see Table 2. Two samples of Ornellas were tested under confinement: one in a cylinder of gold, the other in a cylinder of alumina (Al_2O_3). A third sample (26 g) was without confinement. It is interesting to see that the unconfined large TNT charge (300 g TNT + 29 g booster) exhibits nearly the same reaction products as the small charge (22 g) confined in gold, but is very different from the unconfined small TNT charge (26 g). This leads to the conclusion that for a large charge with a diameter of about 50 mm, argon behaves as a confining medium.

Charges with 45 % TNT/55 % NQ

In order to determine the influence of different argon pressures on the detonation products of cast high explosives consisting of 45 % TNT and 55 % spherical nitroguanidine (NQ), experiments were conducted in the containment described. In each case the detonation products of three experiments were analyzed: one in the evacuated containment, the other under 0,05 MPa and the third under 0,1 MPa of argon pressure, see Table 3.

Additionally, three charges of the same mass and the same composition, but in a glass confinement with a thickness of 9 mm were tested, also in vacuum and under 0,05 and 0,1 MPa of argon. The results are listed in Table 4.

The results of the unconfined shots in Table 3 show that the products formed under an evacuated condition are very different from those produced under 0,05 MPa and 0,1 MPa argon.

With increased pressure we see a distinct decrease of H_2 and CO and a strong increase of CO_2 , H_2O and solid carbon (C_s). The enthalpy of detonation (ΔH_{det}) increases markedly from vacuum to 0,05 MPa, but only slightly from 0,05 MPa to 0,1 MPa of argon. The highest value of the gas formation is obtained in vacuum.

It is also of interest to see how the concentrations of NH_3 and HCN increase with a higher argon pressure; the same holds also for CH_4 and C_2H_2 . It seems as if argon behaves as a confinement: It leads to a distinct increase in the heat of detonation because of the increase of the species representative of a lower-temperature isentrope such as CO_2 , H_2O and solid carbon (C_s) and a corresponding decrease of the species representative of a higher temperature isentrope: CO and H_2 ²⁾

From vacuum to 0,1 MPa of argon, the enthalpy of reaction increases from 2 999 to 3 763 kJ/kg by 20,6 %. On the other hand, the glass confined charge exhibits at 0,1 MPa of argon a value of 4003 kJ/kg, which corresponds to an increase of only 6,4 %, compared with the unconfined charge at the same pressure, see Tables 3 and 4.

In order to study the effects of argon in more detail, detonation products for argon confinement at 0,2 and 0,3 MPa were also analyzed. The results are listed in Table 5. As we see, an additional pressure of argon (0,2 MPa) increases the heat of reaction only by 27 kJ, and a further pre-pressurization to 0,3 MPa exhibits no additional improvement of the heat output.

Analysis of Soot

After each shot, the residue in the containment was collected by using a dust cleaner, dried and then analyzed for carbon, hydrogen and nitrogen by combustion analysis. For comparison, the carbon residue was also calculated from the mass balance.

Table 6 lists the elemental analysis of the soot as well as the analyzed and calculated amounts of carbon. The carbon content clearly increases when going from vacuum to 0,05, 0.1 and 0.2 MPa of argon.

The elemental analysis also shows that the nitrogen content increases when the argon pressure is raised. It is assumed that the formation of substances containing nitrogen increase in the same manner as HCN and NH_3 ⁵⁾.

It is suspected that the formation of diamonds is also favored by a stronger confinement. ⁶⁾

3.2 Reaction Products of PBX

Detonation products of PBX-charges consisting of 80 % RDX with a mean grain size of 10 μm and 20 % of a polybutadiene binder are listed in Table 7. The experiments were conducted in vacuum under 0,05 MPa and 0,1 MPa of argon. The detonation products behave in the same way as discussed before.

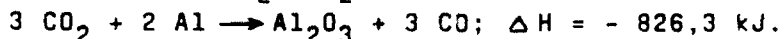
A decrease of H_2 and CO and an increase of CO_2 , H_2O , C_s , NH_3 , HCN, C_2H_2 and CH_4 , going from vacuum to 0,05 and 0,1 MPa of argon. Additionally we see an increase of the enthalpy of reaction and a decrease of gas formation.

The reaction enthalpy is much higher than that of the charge containing 45 % TNT and 55 % of nitroguanidine (NQ). The reason for this is that the enthalpy of formation is much less negative for the RDX containing explosive (- 94,0 kJ/kg than that of 45 TNT/55 NQ with a value of - 646 kJ/kg).

3.3 Reaction Products of PBX Charges Containing Aluminium

In order to find out how complete aluminium (Al) reacts in a detonation process under different pre-pressurization, a high explosive charge consisting of 56 % RDX Class C, 14 % RDX (10 μ m), 15 % Al Alcan 400 and 15 % polybutadiene binder was detonated in vacuum and in argon atmosphere (0,1 MPa). The results are listed in Table 8. We see that the reaction products analyzed under vacuum conditions are much closer to those of 0,1 MPa of argon than obtained in the previously described shots. This means that the influence of argon as a confining medium is reduced by using Al containing high explosives. This behavior can also be derived from the values of the enthalpies of reaction, which only exhibit a difference of 1,5 % between the detonation in vacuum and atmospheric pressure of argon.

Regarding the reaction of Al, the results show an amount of 15 % unreacted Al for the vacuum shot compared with 28 % Al for 0,1 MPa of argon. This means that the amount of unreacted Al is considerably higher when the detonation is performed under 0,1 MPa of argon. The reason for the incomplete Al reaction is the negative oxygen balance of - 69,3 % which is responsible for the very low formation of CO₂. CO₂ is needed for the reaction:



4. Conclusions

It has been shown that the analysis of reaction products formed during the detonation of high explosives in a containment of 1,5 m³ is very useful for understanding the detonation behavior under different conditions.

The influence of confinement on the detonation products and therefore also on the heat of detonation can be evaluated. In addition the completeness of the reaction of aluminium or other ingredients can be analyzed.

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- **) Fraunhofer-Institut für Chemische Technologie
D-7507 Pfinztal 1, FRG

Table 1: Example for the evaluation of the complete detonation products and the heat of detonation of Composition B

9. 2.1989

No. 34/30

COMPOSITION B

EXPLOSIVE MASS: 301.0 [G]

EXPLOSIVE FOIL: 17.5 [G]

RDX BOOSTER: 10.0 [G]

TOTAL MASS: 328.5 [G]

57.563 % HEXOGEN 59.50 %

0.916 % PARAFFINE 1.00 %

36.193 % 2,4,6-TNT 39.50 %

5.327 % EXPLOSIVE FOIL 0.00 %

Heat of formation: -9.5 KCAL/KG = -39.8 KJ/KG

Oxygen balance: -43.62 %

Sum formula: C O N H

2.0519 2.6977 2.1083 2.6409

Soot: 1.0000 0.0000 0.0533 0.0713

[MOL%] ANALYSIS WITH H2O and SOOT [MOL/KG]

H2 : 12.05 7.38 3.23

CH4 : 0.28 0.17 0.08

CO : 33.49 20.51 8.99

CO2 : 15.18 9.29 4.08

N2 : 38.55 23.60 10.35

N2O : 0.00 0.00 0.00

NO : 0.09 0.06 0.02

HCN : 0.37 0.23 0.10

H2O : 21.87 9.59

SOOT : 16.90 7.41

Kp(T) Watergas : 6.540

Δ H det [KJ/KG]: 5002.3

MOL/KG : TOTAL: 43.84 GAS: 36.44 COND.: 7.41

Comparison of mass balance: Theory Experiment

N/C 1.0275 1.0275

N/H 0.7983 0.7983

N/O 0.7815 0.7930

Theor. amount of carbon in residue: 29.0 [G] = 35.9 % of carbon

Table 2: Heats and products of detonation of TNT under varying conditions: Comparison between ICT and LLNL

Sample		ICT 28/30	Detonation Calorimeter D. Ornellas, LLNL		
Confinement		no	Gold	Al2O3	no
Charge:					
Density [g/ccm]		7	1.533	1.533	1.000
Diameter [mm]		50	12.7	12.7	12.7
Weight TNT [g]		300	22	22	26
Booster [g]		29	?	?	?
<hr/>					
Products, [Mol %]	H2	3.4	4.3	4.1	20.4
	CH4	0.2	0.9	1.0	0.1
	CO	17.2	18.5	18.9	53.9
	CO2	9.9	11.7	12.5	0.3
	N2	13.5	12.3	12.6	11.9
	NO	0.07	-	0.01	0.01
	HCN	0.8	1.9	0.5	0.3
	NH3	?	1.5	1.8	0.9
	H2O	19.6	14.9	13.3	3.4
	C _s	35.4	34.0	35.2	8.8
<hr/>					
ΔH_{det} [KJ/Kg]:					
Experimental		-	4576	4480	2437
Calc. from products		4320	4744	4091	2977

**Table 3: Charges of 45% TNT / 55% NQ
in different Ar pressures**

Sample No.	1450/1c	1450/2c	1450/3c
Ar pressure, MPa	Vac.	0.05	0.1
Composition	45% TNT/ 55% NQ		
O2-Balance, %	-47.6		
Charge Weight, g	331	332	331
ΔH_f, KJ/Kg	-661	-662	-657
<u>Products, Mol%:</u>	H2	20.7	8.3
	CH4	0.04	0.1
	CO	32.1	17.9
	CO2	3.7	7.9
	N2	27.5	26.1
	NO	0.1	0.1
	HCN	0.3	3.2
	NH3	0.5	3.0
	C2H2	0.02	0.03
	H2O	10.7	19.6
	C_s	4.4	13.8
ΔH_{det}, KJ/Kg	2999	3653	3763
C in Residue [% of total C]	10.8	32.2	35.7
Gas formation [mol/Kg]	44.5	37.9	35.7

Table 4: Charges of 45% TNT / 55% NQ in glass confinement and different Ar pressures

Sample No.	1451/1	1451/2	1451/3
Ar pressure, MPa	Vac.	0.05	0.1
Composition	45% TNT/ 55% NQ		
O ₂ -Balance, %	-47.6		
Charge Weight, g	332	335	332
ΔH_f , KJ/Kg	-656	-658	-658
<u>Products, Mol%:</u>			
H ₂	8.7	4.2	3.1
CH ₄	0.2	0.4	0.44
CO	15.9	10.2	9.3
CO ₂	7.9	11.9	12.7
N ₂	27.3	26.0	25.6
NO	0.06	0.05	0.14
H ₂ CN	1.35	2.4	1.1
NH ₃	1.15	4.7	5.3
C ₂ H ₂	0.07	0.1	0.13
H ₂ O	20.5	20.7	21.0
C _s	16.8	19.2	21.3
ΔH_{det} , KJ/Kg	3779	3960	4003
C in Residue [% of total C]	39.8	43.3	47.2
Gas formation [mol/Kg]	37.1	34.4	33.0

**Table 5: Charges of 45% TNT / 55% NQ in
Ar pressures of 0.1 to 0.3 MPa**

Sample No.	1450/3c	1450/2b	1450/3b
Ar pressure, MPa	0.1	0.2	0.3
Composition	45% TNT/ 55% NQ		
O ₂ -Balance, %		-47.6	
Charge Weight, g	331	328	327
ΔH_f , KJ/Kg	-657	-648	-646
<u>Products, Mol%:</u>			
H ₂	5.0	4.2	4.4
CH ₄	0.2	0.3	0.35
CO	14.3	11.4	11.4
CO ₂	10.3	10.7	11.3
N ₂	25.6	25.2	24.8
NO	0.13	0.22	0.3
N ₂ O	-	0.5	0.8
H ₂ CN	3.6	1.4	1.0
NH ₃	4.9	3.4	3.6
C ₂ H ₂	0.1	0.1	0.1
H ₂ O	20.0	21.7	20.8
C _s	15.9	20.8	21.2
ΔH_{det} , KJ/Kg	3763	3790	3706
C in Residue [% of total C]	35.7	46.4	46.6
Gas formation [mol/Kg]	35.7	33.4	32.8

Table 6: Analysis of the residual soot of the charges
45% TNT / 55% NQ

Sample No.	Ar pressure [MPa]	C %	H %	N %	Total Carbon [g]	
					analysed	calculated
1450/1c	Vacuum	87.3	1.0	10.4	5.9	8.1
1450/2c	0.05	86.9	1.1	12.0	20.9	24.2
1450/3c	0.1	85.4	1.3	13.3	31.6	26.6
1450/1b	0.1	82.4	1.7	15.9	31.7	36.6
1450/2b	0.2	73.1	2.4	24.5	36.1	34.6
1450/3b	0.3	68.9	2.8	28.2	35.6	34.6

Table 7: PBX charges with 80% RDX / 20% PB

Sample No.	HX 72/1	HX 72/2	HX 72/3
Ar pressure, MPa	Vacuum	0.05	0.1
Composition	20% PB / 80% RDX (10 μ m)		
O ₂ -Balance, %	-73.3		
Charge Weight, g	329	328	330
ΔH_f , KJ/Kg	-94	-90	-95
<u>Products, Mol%:</u>			
H ₂	33.5	15.0	12.3
CH ₄	0.1	0.7	2.9
CO	34.4	17.3	13.1
CO ₂	1.2	3.5	6.6
N ₂	18.8	18.0	18.8
NO	0.05	0.03	0.02
HCN	0.1	0.8	0.9
NH ₃	0.5	2.9	2.8
C ₂ H ₂	-	0.06	0.5
H ₂ O	4.8	19.6	19.9
C _s	6.6	22.2	22.2
ΔH_{det} , KJ/Kg	2949	4214	4440
C in Residue [% of total C]	15.7	49.9	47.3
Gas formation [mol/Kg]	52.1	42.0	39.7

Table 8: PBX Charges with RDX and Al Alcan 400

Sample No.	HXA 123/1	HXA 123/3
Ar pressure, MPa	Vacuum	0.1
Composition	15% PB/ 15% Al Alcan 400 56% RDX Class C/ 14% RDX (10 μ m)	
O2-Balance, %	-69.3	
Charge Weight, g	331	331
ΔH_f , KJ/Kg	-73	-71
<u>Products, Mol%:</u>		
H2	29.5	25.8
CH4	0.04	1.1
CO	26.1	20.1
CO2	0.01	2.7
N2	16.9	18.1
NO	0.07	0.05
HCN	0.1	2.35
NH3	2.2	0.9
C2H2	0.04	0.3
C2H4	0.03	0.2
H2O	4.2	7.2
Al2O3	4.6	3.9
Al	1.6	3.0
C _s	14.6	14.3
$K_p(T)$?	2.018
Freeze out Temp. [K]		1365
ΔH_{det} , KJ/Kg	5143	5066
C in Residue [% of total C]	35.6	34.5
Unreacted Al, %	15.0	28.0
Gas formation [mol/Kg]	38.6	37.0

SYNTHESIS AND EXPLOSIVE PERFORMANCE CHARACTERISTICS OF POLYNITROPOLYCYCLIC CAGE EXPLOSIVES

ALAN P. MARCHAND,* PENDRI ANNAPURNA, BENNY E. ARNEY, JR., VIJAY R. GADGIL, DAYANANDA RAJAPAKSA, G. V. MADHAVA SHARMA, RAJIV SHARMA, AND UMESH R. ZOPE

*Department of Chemistry
University of North Texas
NT Station, Box 5068
Denton, Texas 76203 U. S. A.*

ABSTRACT: The synthetic methodology which has been utilized to prepare a number of polynitropolycyclic cage explosives in our laboratory is presented, and the underlying strategy is described in each case. The results of thermodynamic studies of several polynitropolycyclic systems are presented and discussed along with preliminary results of explosive evaluation studies which have been performed on D₃-hexanitrotrishomocubane and on 4,4,8,8,11,11-hexanitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane.

1. Introduction

For the past decade, our research group has been involved in an intensive effort to synthesize new polynitropolycyclic "cage" compounds. Such polycarbocyclic compounds, by virtue of their rigid, compact structures, generally pack efficiently in the solid state and thus possess unusually high crystal densities. In addition, their carbocyclic frameworks often possess significant levels of steric strain, which correspondingly render them thermodynamically unstable relative to isomeric non-cage structures.

In recent years, attention has become focused upon the potential use of polycarbocyclic cage compounds as a new class of energetic

materials. In particular, efforts have been expended in several laboratories worldwide to introduce nitro groups as substituents into highly strained cage molecules in an effort to produce high energy density explosives and propellants. Progress in the synthesis and chemistry of polynitropolycyclic cage molecules has been the subject of a recent review (Marchand, 1988).

We now present a summary of our efforts to synthesize novel polynitropolycyclic compounds by (i) reviewing synthetic strategy, (ii) providing examples whereby this strategy has been applied successfully, and (iii) providing the results of theoretical calculations and explosive performance tests. In this way, we hope to demonstrate that polynitropolycyclic cage compounds indeed comprise a new class of relatively powerful, shock-insensitive explosives which are readily amenable to small-scale laboratory synthesis. In addition, the availability of small quantities of these novel energetic materials provides a means by which theoretically predicted values of, e. g., density, heat of formation, detonation pressure, and detonation velocity might be evaluated experimentally.

2. Synthetic Strategy

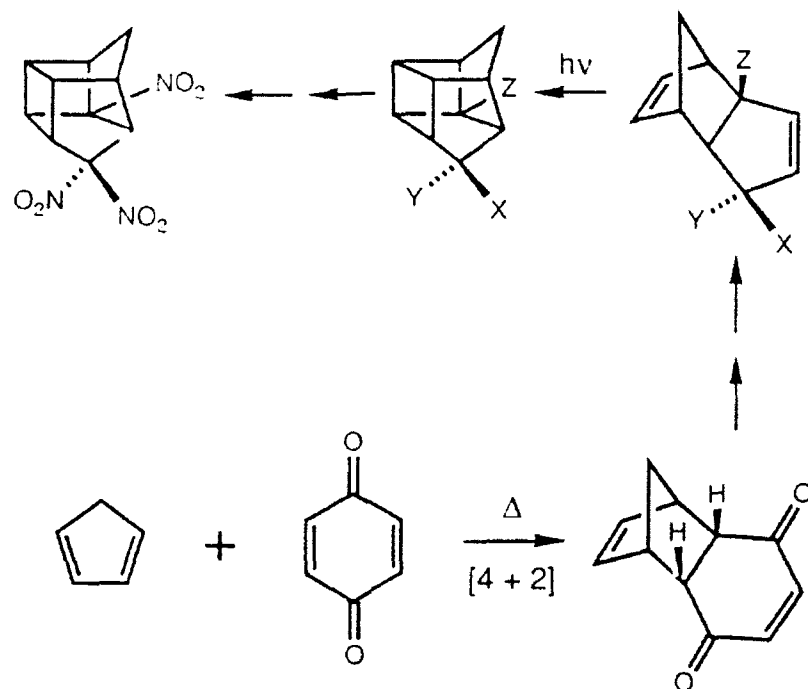
2.1. SYNTHESIS OF *GEM*-DINITRO $[C(NO_2)_2]$ SUBSTITUTED CAGE COMPOUNDS

It is instructive to consider an approach to the synthesis of 3,5,5-trinitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decane, as this was one of the first polynitro cage systems to be synthesized in our laboratory (Marchand and Suri, 1984). A retrosynthetic perspective is shown in Scheme 1.

Two approaches were envisioned initially. Either the nitro groups could be introduced into the molecule at an early stage in the synthesis, or a suitably functionalized cage might be constructed first with subsequent conversion of the substituents (X, Y, and Z) into NO_2 groups at a later stage. The second approach permits a gradual and systematic increase in the degree of nitro substitution in the cage molecule (which is determined by the number and location of the substituents X, Y, and Z in the caged precursor). This approach permits the investigator to gauge the cumulative effects of increasing NO_2 substitution upon the physical and chemical properties of the

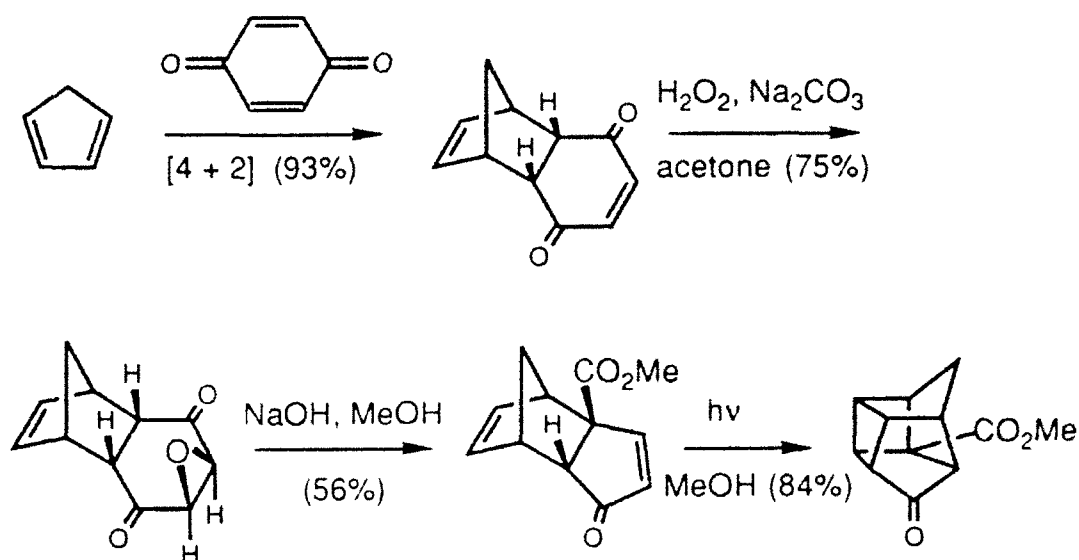
cage system. We have adopted the latter approach in our syntheses of polynitropolycyclic compounds.

Scheme 1
Retrosynthetic Perspective



Since we were aware of multistep procedures by which a C-CO₂H group and a ketone carbonyl group might be converted into C-NO₂ and C(NO₂)₂ groups, respectively, we sought to prepare the corresponding ketoester (i.e., methyl pentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decan-5-one-3-carboxylate). This cage ketoester corresponds to a substituted pentacyclodecane in which Z = CO₂Me and X,Y = O (ketone carbonyl group). It can be synthesized conveniently by using the method which is summarized in Scheme 2.

Scheme 2

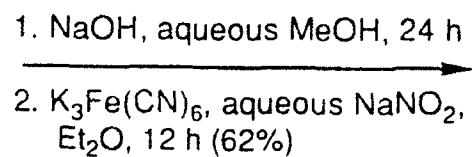
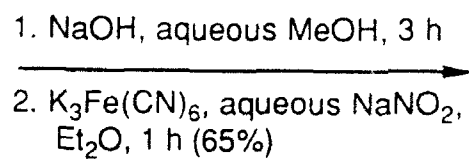
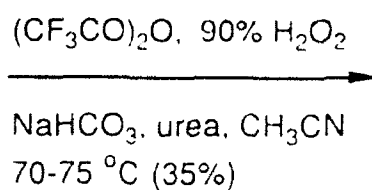
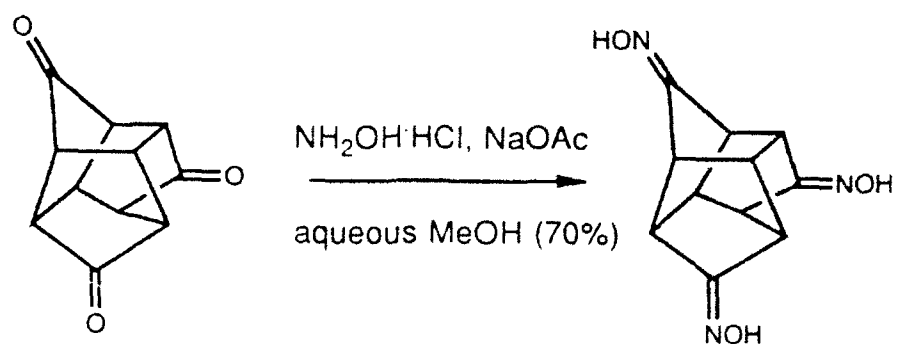


Our synthesis of the desired trinitro cage compound was completed first by converting the ketone $\text{C}=\text{O}$ group in the cage ketoester into $\text{C}(\text{NO}_2)_2$ via the sequence $(\text{C}=\text{O}) / (\text{C}=\text{NOH}) / (\text{CBrNO}_2) / (\text{CHNO}_2) / [\text{C}(\text{NO}_2)_2]$ (Nielsen, 1962; Kornblum, Singh, and Kelly, 1983). Subsequently, the ester functionality was converted into a $\text{C}-\text{NH}_2$ group (Shiori, Ninomiya, and Yamada, 1972), and the resulting primary amine was oxidized by using *m*-chloroperbenzoic acid, thereby completing the synthesis (Marchand and Suri, 1984).

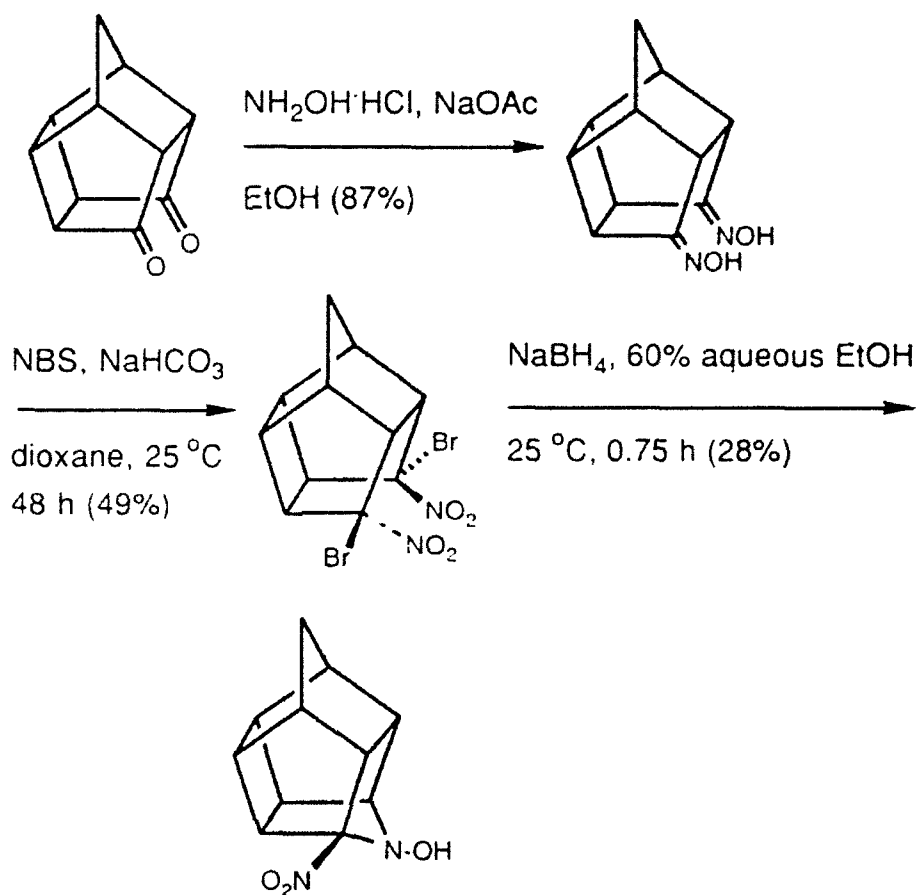
In addition to the sequence described above for converting ketone $\text{C}=\text{O}$ groups into $\text{C}(\text{NO}_2)_2$ functionalities, we have also effected this conversion via oxidative nitration of the corresponding ketoxime. This procedure is exemplified by the conversion of D_3 -tris-homocubane-1,4,7-trione into D_3 -hexanitrotrishomocubane (Scheme 3; Marchand, Sharma, Annapurna, and Pednekar, 1988).

Transannular proximity effects are frequently encountered in cage systems. When they occur, they often lead to unexpected (and occasionally frustrating) side reactions. We encountered such frustration in our initial attempt to synthesize 8,8,11,11-tetrani-tropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane from the corresponding diketone (Scheme 4; Marchand, Arney, Jr., and Dave, 1988).

Scheme 3

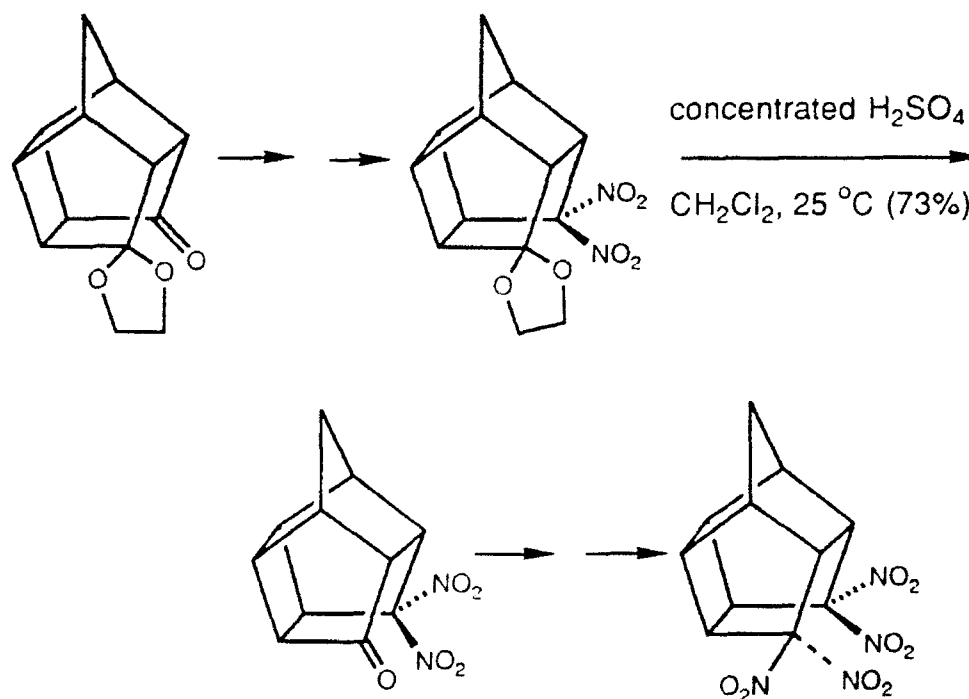


Scheme 4



This difficulty was overcome by converting the cage diketone into its corresponding mono(ethylene acetal), thereby protecting one of the two equivalent ketone $\text{C}=\text{O}$ groups in the substrate. The remaining free $\text{C}=\text{O}$ functionality was converted subsequently into a $\text{C}(\text{NO}_2)_2$ group, thereby affording 11,11-dinitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one ethylene ketal. The ketal functionality was removed by acidic hydrolysis, and the resulting dinitroketone was converted into the target tetranitropentacycloundecane (Scheme 5; Marchand, Arney, Jr., and Dave, 1988).

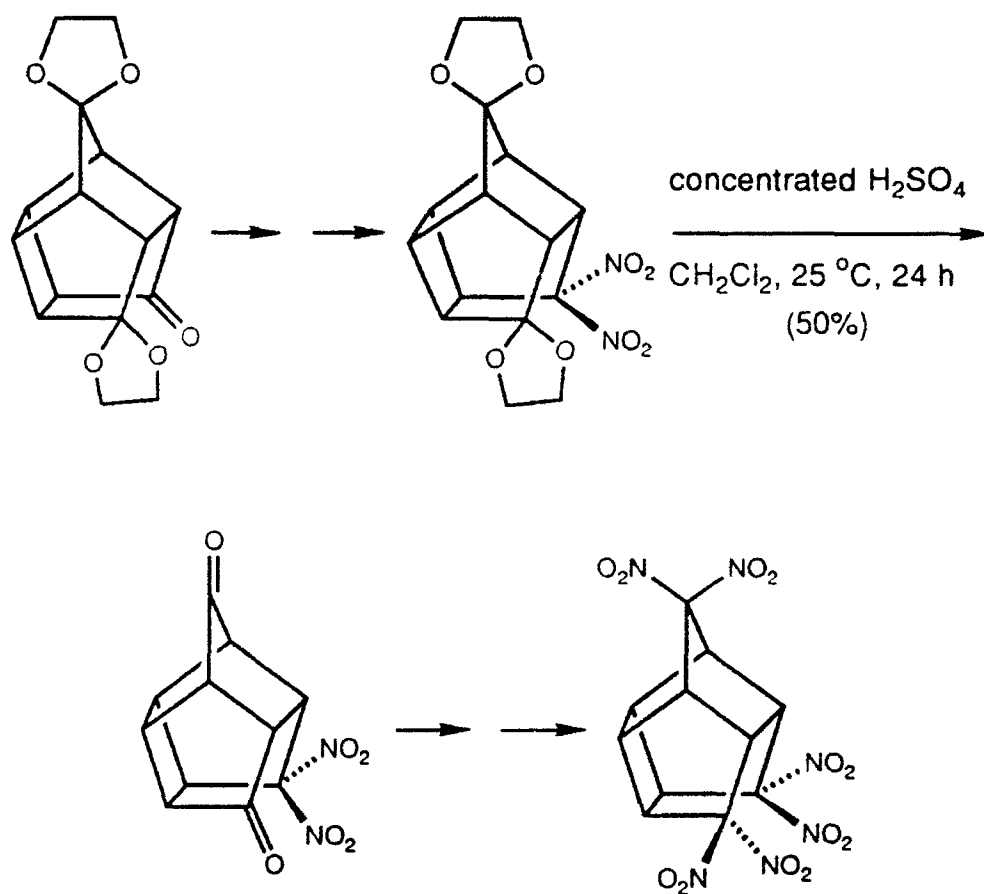
Scheme 5



A similar strategy led to the successful synthesis of 4,4,8,8,11,11-hexanitropentacyclo[5.4.0.0^{2.6}.0^{3.10}.0^{5.9}]undecane (Scheme 6; Marchand, Dave, Rajapaksa, Arney, Jr., Flippen-Anderson, Gilardi, and George, 1989).

The X-ray crystal structure of 4,4,8,8,11,11-hexanitropentacyclo[5.4.0.0^{2.6}.0^{3.10}.0^{5.9}]undecane has been obtained. The crystal density of this compound calculated from the X-ray data was found to be 1.827 g-cm⁻³ (Marchand, Dave, Rajapaksa, Arney, Jr., Flippen-Anderson, Gilardi, and George, 1989). This value compares favorably with the previously calculated value of 1.836 g-cm⁻³ (Sandus, 1985).

Scheme 6

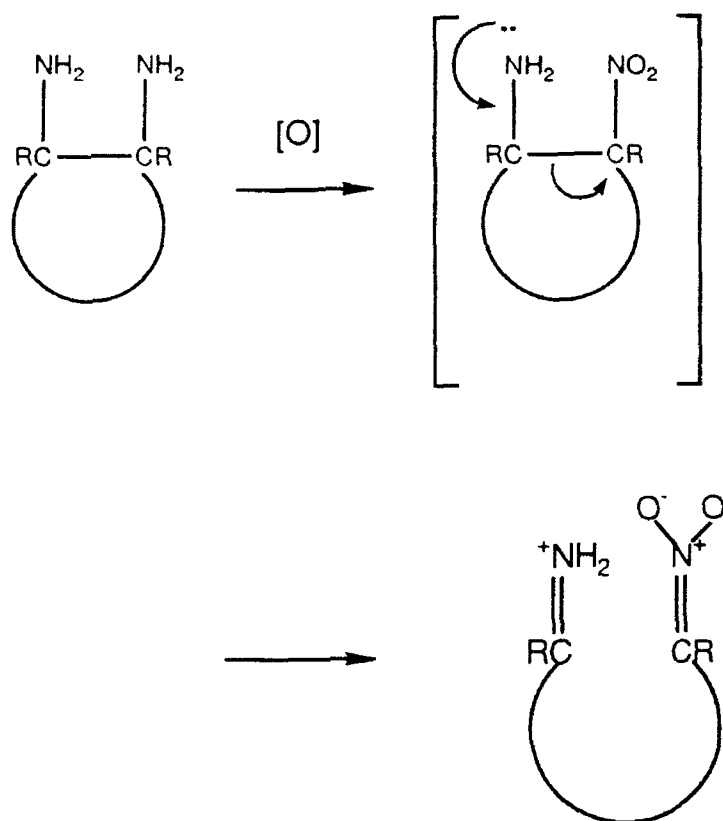


2.2. SYNTHESIS OF VIC-DINITRO $[\text{R}_2\text{C}(\text{NO}_2)\text{-C}(\text{NO}_2)\text{R}_2]$ SUBSTITUTED CAGE COMPOUNDS

A special situation is incurred when contemplating the synthesis of *vic*-dinitro systems, $\text{R}_2\text{C}(\text{NO}_2)\text{-C}(\text{NO}_2)\text{R}_2$. In general, the preparation of $\text{R}_3\text{C-NO}_2$ groups via oxidation of the corresponding primary amine, $\text{R}_3\text{C-NH}_2$, proceeds smoothly under a variety of experimental conditions (Eaton, et al, 1984; Zajac, Jr., Walters, and Woods, 1989; Murray, Rajadhyaksha, and Mohan, 1989). However, a comparable approach to *vic*-dinitro systems necessarily proceeds via an intermediate β -nitroamine, which electronically is a "push-pull" system. The C-C σ -bond which intervenes between the C- NO_2 and C- NH_2 groups in this intermediate is subject to Haller-Bauer type cleavage (Hamlin and Weston, 1957). This is expected to present a particularly vexing problem in highly strained cage systems, where relief of

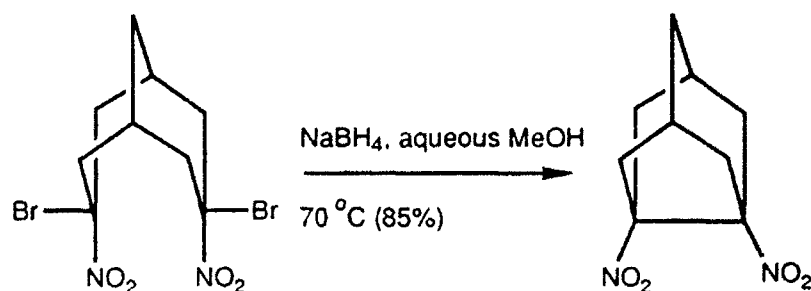
steric strain provides an important driving force for ring cleavage (Scheme 7).

Scheme 7



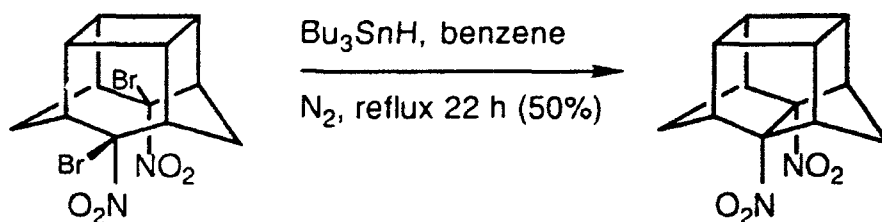
Nevertheless, methods have been developed for synthesizing *vic*-dinitro compounds which circumvent this complication. Thus, sodium borohydride reduction of 3,7-dibromo-3,7-dinitrobicyclo[3.3.1]nonane results in reductive coupling, thereby affording 3,7-dinitro-noradamantane (Scheme 8: Klimova, et al., 1974).

Scheme 8



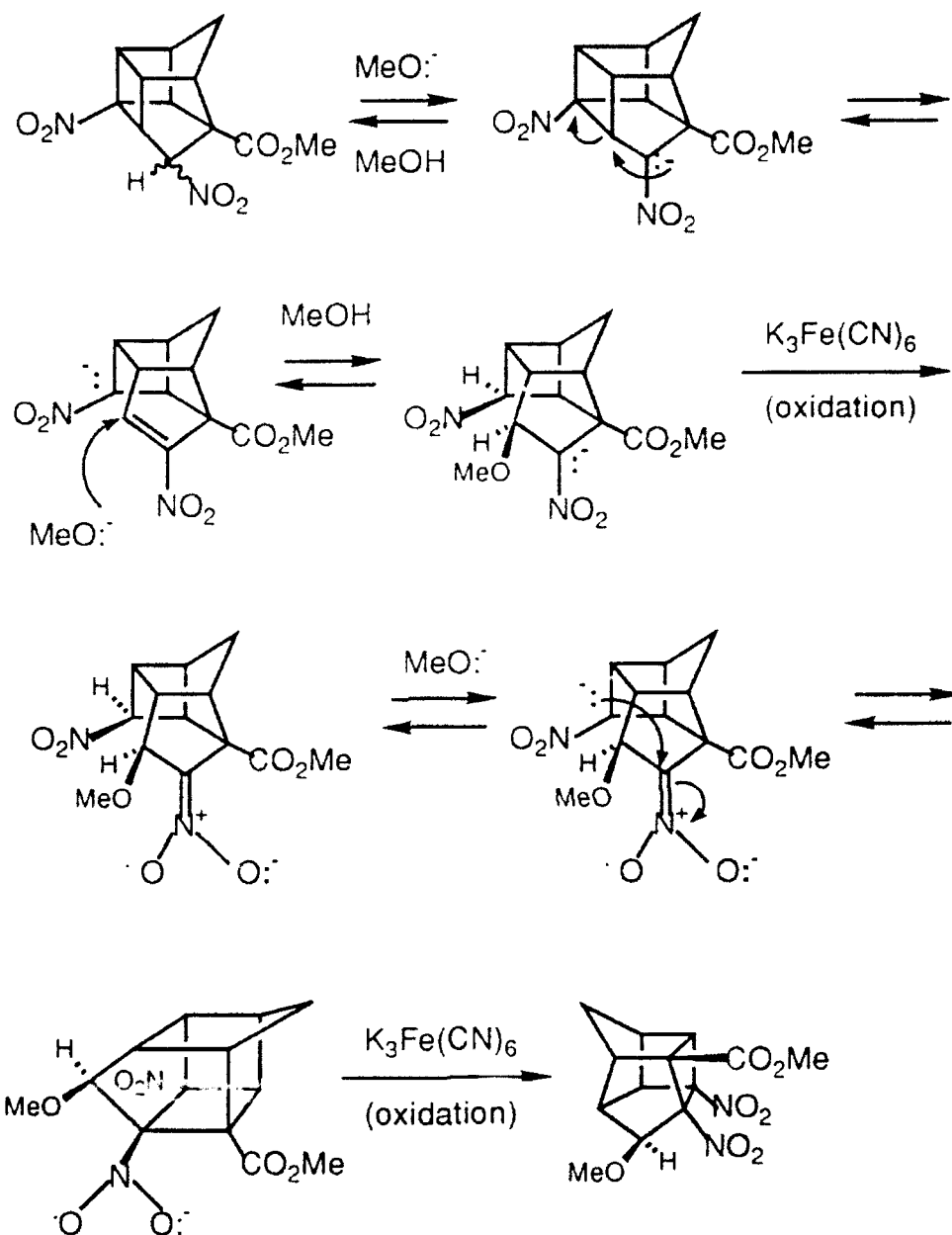
This same product has been observed to accompany the formation of 3,7-dibromo-3,7-dinitrobicyclo[3.3.1]nonane via oxidative bromination of bicyclo[3.3.1]nonane-3,7-dione dioxime with 1,3-dibromo-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (Walters, Zajac, Jr., and Woods, 1991). In addition, Paquette and coworkers have synthesized 2,6-dinitrohexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane via a trialkyltin hydride promoted reductive cyclization (Scheme 9: Paquette, Fischer, and Engel, 1985).

Scheme 9



An entirely different approach to the synthesis of a *vic*-dinitro substituted cage compound arose during an attempt to promote oxidative nitration of a CHNO_2 group in a substituted 1,3-bishomocubane. The desired oxidative nitration process was accompanied by a deep-seated skeletal rearrangement, thereby resulting in an unexpected synthesis of a *vic*-dinitro substituted 1,3-bishomocubane (Scheme 10: Marchand, Jin, Flippen-Anderson, Gilardi, and George, 1987).

Scheme 10

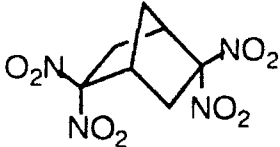

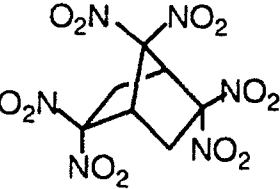


3. PROGRESS TOWARD THE SYNTHESIS OF 2,2,5,5,7,7-HEXANITRONORBORNANE

Recent efforts in our laboratory have been directed toward the synthesis of 2,2,5,5,7,7-hexanitronorbornane. This molecule was

chosen as a synthetic target primarily on the basis of computational results, which are summarized in Table 1 (Jayasuriya, 1990).

Table 1. Thermodynamic Calculations for Polynitronorbornanes

Compound	Density (g-cm ⁻³)	ΔH_f (kcal/mol)	P_{CJ} (kBar)	D (m/sec)
	1.80 (1.71, X-ray)	+32	308	8137
	1.81	+35	330	8174
	1.90	+72	410	8914

Calculations performed by Dr. Keerthi Jayasuriya, GEO-Centers, Inc., Picatinny Arsenal, NJ. Values for HMX: P_{CJ} = 389 kBar; D = 9130 m./sec.

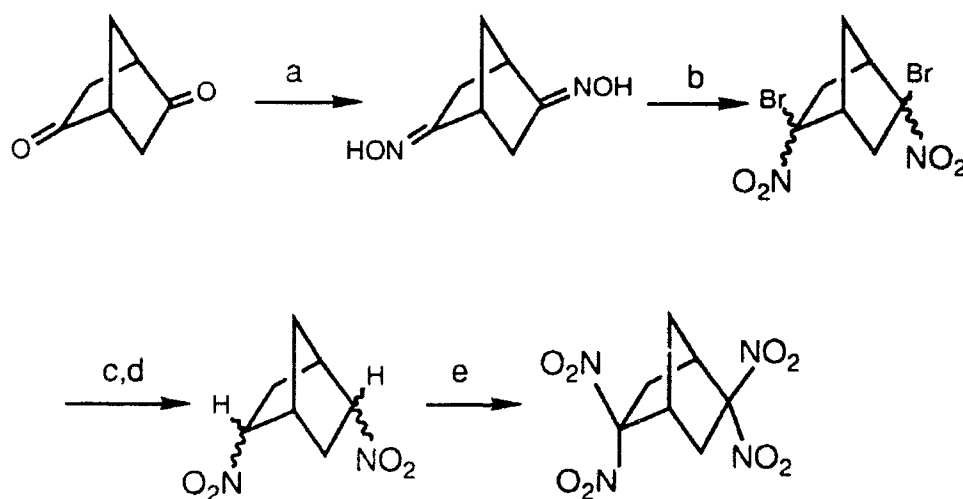
We envisioned some potentially serious problems when contemplating rational approaches to the synthesis of this polynitronorbornane. Inspection of molecular models suggests that there may be considerable steric crowding in 2,2,5,5,7,7-hexanitronorbornane brought about by nonbonded interactions between the (*exo*-2-) - (*syn*-7-) nitro groups on one hand and the (*exo*-5-) - (*anti*-7-) nitro groups, respectively, on the other. Also, the potential for Haller-Bauer cleavage (Hamlin and Weston, 1957) of

this strained bicyclic system exists were the selected synthetic route to proceed by way of an intermediate which contains a 1,3-dione moiety. For these reasons, we initiated two model studies wherein the syntheses of 2,2,5,5- and 2,2,7,7-tetranitronorbornane were undertaken. In this way, we hoped to be able to address the problems noted above and thereby improve our chances of reaching the target hexanitronorbornane via rational synthesis.

3.1. SYNTHESIS OF 2,2,5,5-TETRANITRONORBORNANE

A straightforward synthesis of 2,2,5,5-tetranitronorbornane is shown in Scheme 11 (Marchand, Sharma, Zope, Watson, and Kashyap, 1992; Olah, Ramaiah, Surya Prakash, and Gilardi, 1992). This synthesis contains yet another example of successful multistep conversion of a ketoxime into a $C(NO_2)_2$ group.

Scheme 11



(a) NaOAc, MeOH, $NH_2OH \cdot HCl$, 25 °C, 24 h (94%); (b) NBS, $NaHCO_3$, dioxane, 25 °C, 14 h (36%), (c) $NaBH_4$, 80% aqueous EtOH, 0 °C to 25 °C, followed by (d) 20% aqueous HOAc (98%); (e) $K_3Fe(CN)_6$, $NaNO_2$, KOH, aqueous MeOH (91%).

3.2 SYNTHESIS OF 2,2,7,7-TETRANITRONORBORNANE

Our synthesis of 2,2,7,7-tetranitronorbornane is shown in Scheme 12 (Marchand, Sharma, Zope, Watson, and Kashyap, 1992). The approach shown therein was chosen to avoid the intermediacy of norbornan-2,7-dione, for which Haller-Bauer cleavage under either acidic or basic conditions was considered to be a potentially serious problem. Indeed, when a solution of 7,7-dimethoxynorbornan-2-one (one of the intermediates in Scheme 12) in 10% aqueous H_2SO_4 -THF was refluxed for 7 h, Haller-Bauer cleavage indeed occurred concomitant with hydrolysis of the ketal group, thereby affording 3-oxocyclohexanecarboxylic acid. None of the desired product of simple ketal hydrolysis, i.e., norbornane-2,7-dione, could be isolated from this reaction.

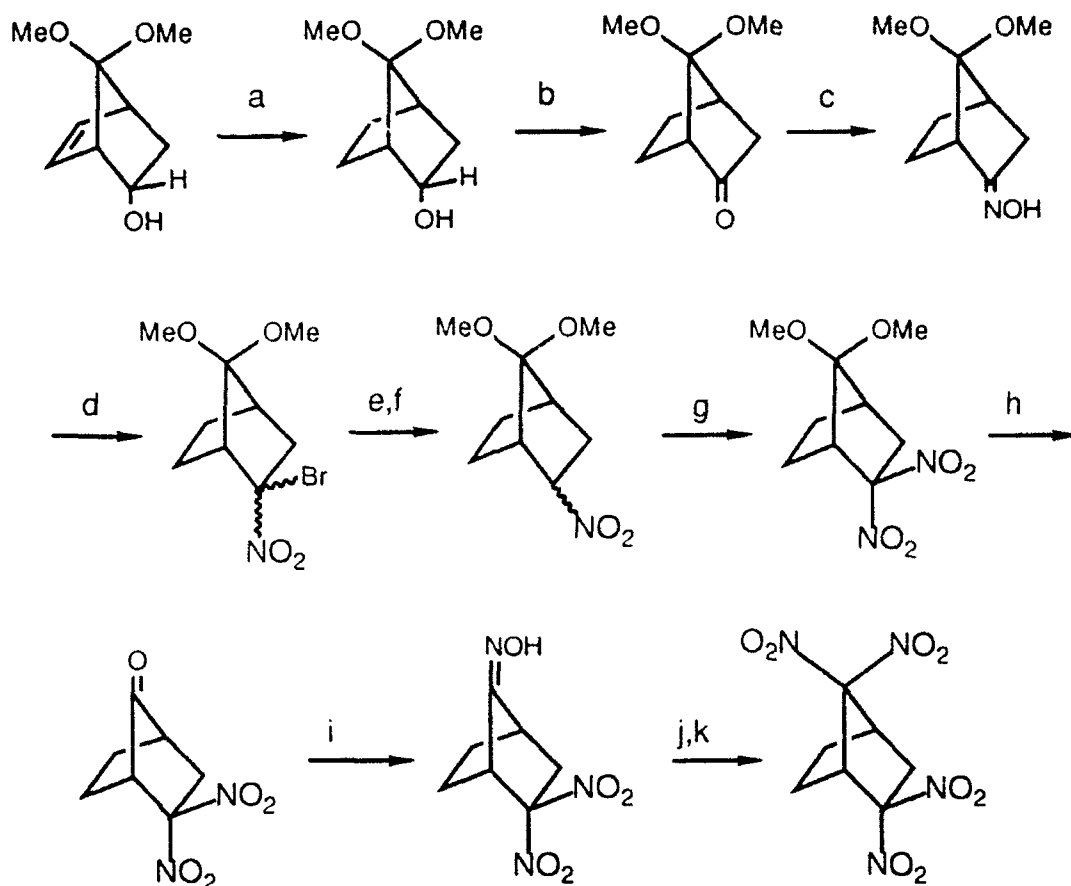
The proton NMR spectrum of 2,2,7,7-tetranitronorbornane contains an interesting feature which merits comment. The C(1) bridgehead proton in this compound is unusually highly deshielded (δ 4.4). Similar deshielding of the C(3) bridgehead proton in 2,2,4,4-tetranitroadamantane (δ 4.7) has been reported (Dave, Ferraro, Ammon, and Choi, 1990). This unusual deshielding might simply reflect the operation of cumulative magnetic anisotropy effects of the adjacent NO_2 groups in both of these compounds. Alternatively, deshielding of the bridgehead proton (which is flanked by four NO_2 groups, in each case) in each of these compounds might simply reflect the cumulative electron withdrawing inductive effect of the nitro substituents. The source of this unusual deshielding effect upon the C(1) bridgehead proton in 2,2,7,7-tetranitronorbornane is undergoing further investigation in our laboratory.

4. Results of Thermochemical Studies and Explosive Performance Tests of Polynitropolycyclic Cage Compounds

4.1. 4,4,7,7,11,11-HEXANITROPENTACYCLO[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]UNDECANE (D₃-HEXANITROTRISHOMOCUBANE) AND 4,4,8,8,11,11-HEXANITROPENTACYCLO[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]UNDECANE

Calculated thermodynamic parameters and density values for these two hexanitropentacycloundecanes are given in Table 2 (Sandus, 1985).

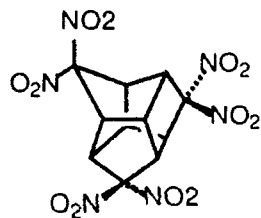
Scheme 12



(a) H_2 (30 psig), 5% Pd-C, EtOAc, 25 °C, 40 minutes (93%); (b) PCC, CH_2Cl_2 , 25 °C, 2 h (95%); (c) NaOAc, MeOH, $\text{NH}_2\text{OH}\cdot\text{HCl}$, 25 °C, 34 h (92%); (d) NBS, NaHCO_3 , aqueous dioxane, 25 °C, 20 h (81%); (e) NaBH_4 , 80% aqueous EtOH, 0 °C to 25 °C, followed by (f) 20% aqueous HOAc (81%); (g) $\text{K}_3\text{Fe}(\text{CN})_6$, NaNO_2 , KOH, aqueous MeOH (67%); (h) concentrated H_2SO_4 , CH_2Cl_2 , 25 °C, 20 minutes (72%); (i) NaOAc, MeOH, $\text{NH}_2\text{OH}\cdot\text{HCl}$, 25 °C, 40 h (100%), (j) 98% red HNO_3 , CH_2Cl_2 , urea, NH_4NO_3 , reflux 0.5 h, followed by (k) 30% aqueous H_2O_2 , reflux 15 minutes (52%).

In Table 3, the results of shock sensitivity tests on D₃-hexanitrotrishomocubane are compared with those obtained for TNT samples.

Table 3. Results of shock sensitivity tests for 4,4,7,7,11,11-hexanitropentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane and for TNT^a (Velicky, Iyer, Campbell, Sandus, Alster, Marchand, Sharma, and Annapurna, 1988)

Compound	Sample weight (mg)	Taper diameter (in.)		Taper Angle (Degrees) ^b
		Initial	Final	
TNT	36.4	0.153	0.165	3.9
TNT	36.8	0.153	0.167	4.4
TNT	37.1	0.154	0.167	4.1
	38.1	0.145	0.154	2.9

^aA constant stimulating voltage of 12 kV was employed.

^bThe taper angle is the angle which the inclined face of the taper makes with the vertical.

The data in Table 3 reveal that detonation of D₃-hexanitrotrishomocubane produces smaller initial and final taper diameters than does detonation of TNT when the same stimulus is applied to either sample. This result indicates that D₃-hexanitrotrishomocubane is less shock sensitive than is TNT. In addition, detonation of D₃-hexanitrotrishomocubane produces a smaller taper angle than does detonation of TNT. Hence, the propagation rate is slower in D₃-hexanitro-

trishomocubane than in TNT (Velicky, Iyer, Campbell, Sandus, Alster, Marchand, Sharma and Annapurna, 1988).

As part of this study, a plot of relative energy delivery (%) vs. V/V_0 was prepared, where relative energy delivery is the percent energy difference between the isentropic expansion of the gaseous products of an explosive and that of TNT. It is expressed at various ratios, V/V_0 , of the specific volume of the gaseous products to that of the intact explosive. The plot thereby obtained indicates that the energy output of D₃-hexanitrotrishomocubane is, at most, 5% below that of "Comp. B". It should be noted that both D₃-hexanitrotrishomocubane and Comp. B are substantially more powerful explosives than TNT.

Thermal analysis of D₃-hexanitrotrishomocubane was performed by using differential scanning calorimetry (DSC). A DSC thermogram of a 3.34 mg sample of this compound was obtained by heating the sample at 10 °C/minute. An exothermal reaction begins at 272 °C, reaches a maximum at 308 °C, and ends at 331 °C. A second, smaller exotherm begins at 331 °C, reaches a maximum at 338 °C, and is completed at 355 °C. The heat of the two reactions is -255.9 and -20.0 cal/g, respectively (Campbell, 1987).

Shock sensitivity tests were also performed on 4,4,8,8,11,11-hexanitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane by using the exploding foil slapper technique described above. Once again, a plot of relative energy delivery vs. V/V_0 was prepared, so that the explosive performance of this compound could be compared with that of TNT. The results of these studies indicate that the explosive power of 4,4,8,8,11,11-hexanitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane is *ca.* 37% greater than that of TNT. In comparison, the corresponding test results obtained for D₃-hexanitrotrishomocubane indicate that this material is slightly less powerful (i.e., its explosive performance is *ca.* 34% greater than that of TNT). Importantly, the former compound is a considerably less sensitive explosive than the latter (relative to TNT). It must be emphasized that these conclusions are tentative and are based upon a limited number of experiments performed on small quantities of materials (<50 mg, in each case; Campbell, 1991).

4.2. POLYNITROPENTACYCLO[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]DECANES

The results of DSC thermal analysis of some di-, tri-, and tetranitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decanes are compared with those for the parent cage hydrocarbon (i. e., 1,3-bishomocubane) in Table 4 (Weinstein, Alster, and Marchand, 1986). The data in Table 4 suggest that all of these polynitro cage compounds have high thermal stabilities relative to that of the parent cage hydrocarbon. In addition, the apparent activation energy for thermal decomposition of 5,5-dinitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]-decane-3-carboxylic acid was determined to lie in the range 202-210 kJ-mol⁻¹.

4.3. 2,2,5,5- AND 2,2,7,7-TETRANITRONORBORNANES

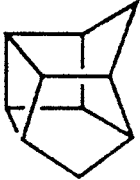
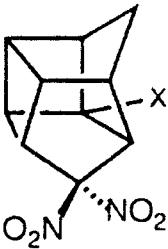
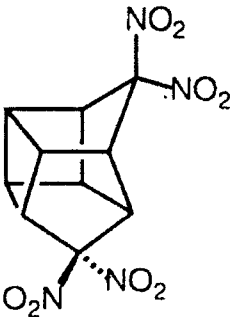
DSC thermal analyses of these two tetranitrobornanes have been obtained recently (Campbell, 1991). 2,2,5,5-Tetranitronorbornane displays an exotherm onset at *ca.* 230 °C which reaches a maximum at *ca.* 250 °C. However, 2,2,7,7-tetranitronorbornane displays somewhat lower thermal stability; its exotherm onset occurs at 216 °C and reaches a maximum at 224 °C. The heat of this latter process was calculated to be -771.5 cal/g (Campbell, 1991).

5. Summary and Conclusions

Several polynitropolycyclic compounds have been synthesized in our laboratory during the past decade under U. S. Army sponsorship. The results of theoretical calculations, borne out by the results of thermal analysis (DSC) and explosive performance evaluation tests on small quantities of our materials, suggest that D₃-hexanitro-trishomocubane and 4,4,8,8,11,11-hexanitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane are both more powerful *and* less sensitive explosives than TNT.

Recent successful syntheses of 2,2,5,5- and 2,2,7,7-tetranitronorbornanes have provided a way in which Haller-Bauer cleavage of strained 1,3-diketones can be avoided by using "1,3-diketone equivalents" as intermediates in the synthesis of somewhat strained RC(NO₂)₂-CHR-CR(NO₂)₂ units. In the future, we plan to apply this methodology to synthesize 2,2,5,5,7,7-hexanitronorbornane, which is predicted to be a powerful and relatively insensitive explosive.

Table 4. Thermal properties of polynitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decanes
(Weinstein, Alster, and Marchand, 1988)

Compound	Transition temperature (°C)	Melting temperature (°C)	Decomposition temperature (°C)
	No transition in the range -30 °C to melting point	138.6	168
 X = CO ₂ H	No transition in the range 50 °C to melting point	137.2	268
X = NO ₂	66.9	201.1	291
	97.9	147.5	279

6. Acknowledgment

I gratefully acknowledge my capable coworkers whose names appear in the list of references and whose untiring efforts made possible the fulfillment of the syntheses which appear in this brief account. Our work on the synthesis of high energy density materials has received financial support during the past decade from the United States Army Armament Research, Development, and Engineering Center, Picatinny Arsenal, NJ, GEO-CENTERS, Inc., Lake Hopatcong, NJ, the Air Force Office of Scientific Research, and the Robert A. Welch Foundation (Grant B-963). This account was written during the tenure (Summer, 1992) of an Erskine Fellowship in the Department of Chemistry, University of Canterbury, Christchurch, New Zealand. I am grateful to the University of Canterbury for the award of this Fellowship and to my host, Professor James M. Coxon, and his colleagues in the Department of Chemistry for their having kindly extended warm hospitality and the use of their excellent facilities to me during this period. Special thanks are due to Dr. Peter J. Steel who read and constructively criticized the manuscript. Finally, I thank my wife, Dr. Nancy Wu Marchand, for her love and continuing support.

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DIAGNOSTIC SCHEME FOR POLYNITROCAGE COMPOUNDS

T. H. CHEN AND C. CAMPBELL

*U. S. Army Armament Research, Development, and
Engineering Center Picatinny Arsenal, New Jersey
07806-5000, U. S. A.*

ABSTRACT. The general schemes for deducing the molecular weight and the structural features of polynitrocage compounds by direct exposure probe mass spectrometry (DEPMS) in the positive ion chemical ionization (PICl) mode using methane as the reagent gas are described.

1. Introduction

In the last several years, we have been developing a diagnostic scheme for the identification of non-volatile and labile unknowns, in particular, the explosives and propellants, using DEPMS. This was necessitated by the large numbers of unknowns which needed to be identified. The specimens included foreign munitions of diverse origins, environmental samples, unknown wastes, and unknown synthetic intermediates.

2. Experimental

2.1. APPARATUS

A Finnigan OWA 1020B gas chromatograph/mass spectrometer (GC/MS) was employed.

2.2. DEPMS

The mass spectrometer was operated in the positive ion chemical ionization (PICI) mode using methane as the reagent gas. For sample introduction, several droplets of the sample solution in acetone with a concentration of approximately 1 mg/ml were carefully deposited on the loop of the heating wire. The solvent was allowed to evaporate at room temperature.

The dried sample was introduced into the ion source of the mass spectrometer through the direct solid insertion probe inlet and the scanning program initiated just prior to the insertion of the sample into the ion source, in order to prevent possible loss of more volatile species. The methane gas pressure in the ion source was maintained at slightly above 3.0 Torr. Immediately following the insertion of the sample into the ion source, the sample was heated rapidly at the rate of 10 mA/sec, corresponding approximately to 10 °C/sec, to 1 A. The analysis time was approximately 100 seconds. The direct exposure probe was then backed off from the ion source and flash heated for several seconds at about 1.35 A to clean the heating wire.

3. Results and Discussion

3.1. DIAGNOSTIC SCHEME

The molecular weight and the structural features are two crucial pieces of information needed in the identification of unknowns. For several years, we have been developing a general scheme which will enable us to rapidly obtain such information using DEPMS. The latter was chosen because of its capabilities for handling highly non-volatile and labile compounds and its speed of analysis.

In the last several years, we have identified or confirmed numerous new polynitrocage compounds and related synthetic intermediates. The compounds studied included polynitrocyclopropane, azitidine, cubane, noradamantane, adamantane,

pentacycloundecane, and others [see for example, Reference 1]. From these studies, the following general scheme has been derived. This represents possible diagnostic ions which could be used in deducing the molecular weight of the sample of interest.

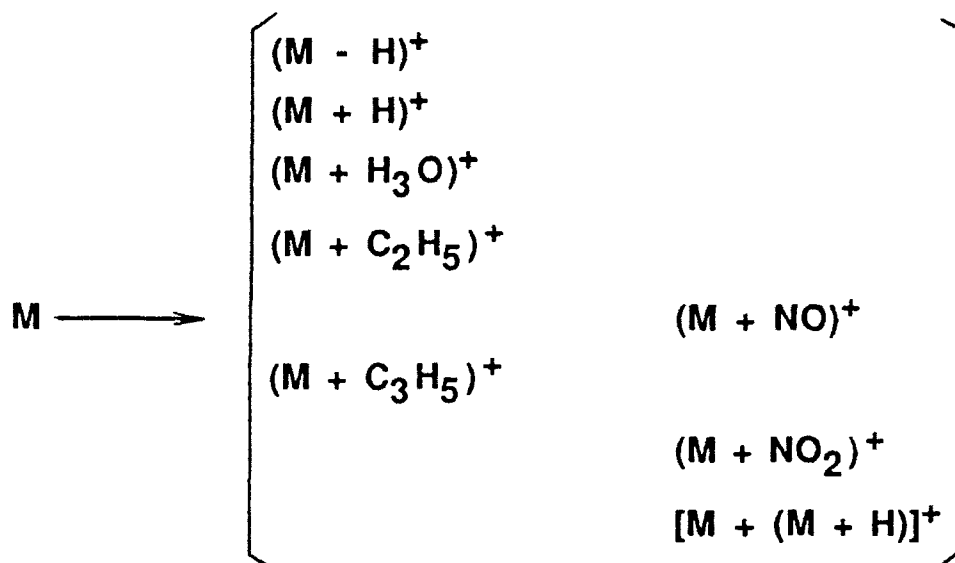


Figure 1. A General Scheme for the Formation of Diagnostic Ions

In general, $(\text{M} + \text{H})^+$ is formed in all cases in relatively good abundance except the very highly nitrated compounds such as 4, 4, 8, 8, 11, 11-hexanitropentacycloundecane. The formation of $(\text{M} - \text{H})^+$ was observed only in the case of 1-trinitromethyladamantane. Further, $(\text{M} + \text{H})^+$ has, in general, considerably higher abundance than other diagnostic ions. In a few instances, the formations of $[\text{M} + (\text{M} + \text{H})]^+$ have been observed. In fact, 1, 2-dinitronoradamantane forms this ion quite easily with an abundance of approximately 50 %. The observation of the $[\text{M} + (\text{M} + \text{H})]^+$ considerably increases the confidence in the molecular weight assignment. It should be noted that many solvents form

this ion quite easily under the DEPMS conditions we employed.

The formations of $(M + \text{NO})^+$ and $(M + \text{C}_3\text{H}_5)^+$ were established at least in the case of dinitrocubane by high resolution DEPMS [1].

3.2. FRAGMENTATION PATTERN

Aside from providing many diagnostic ions, DEPMS also provides structural information in most cases. Following is a general pattern for the fragmentation of polynitrocage compounds:

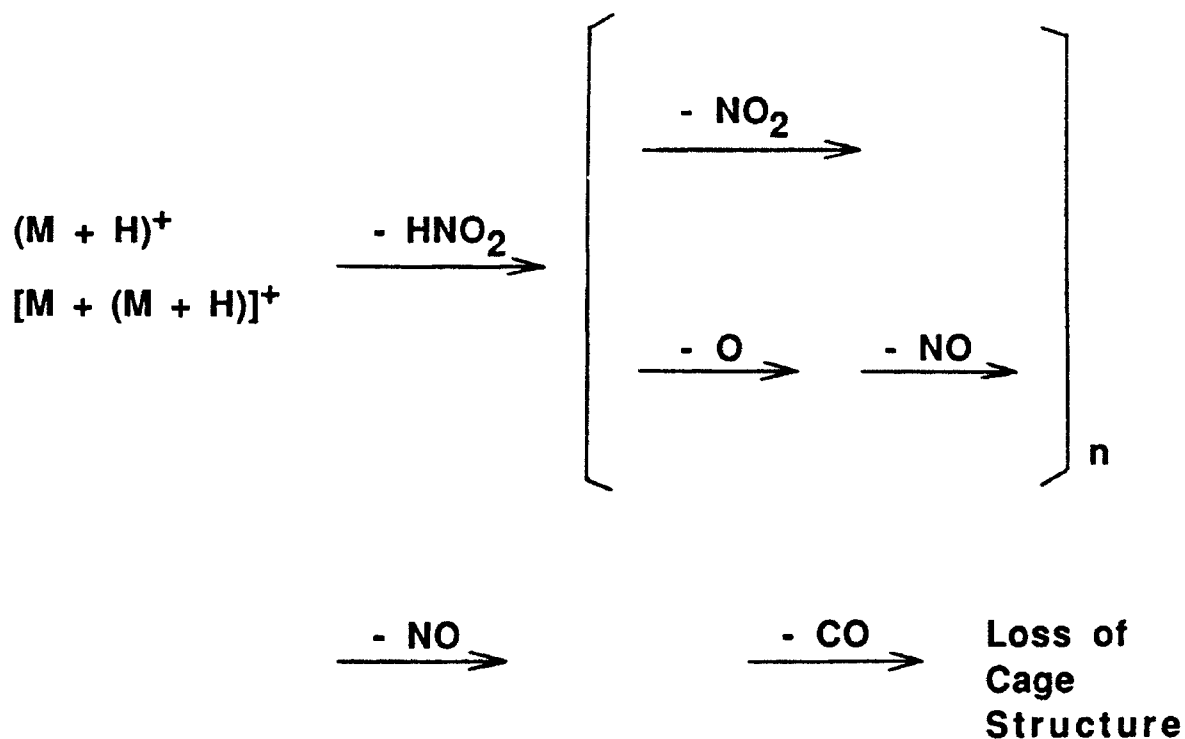


Figure 2. Fragmentation Mechanism of Polynitrocage Compounds

It is interesting to note that $(M + H)^+$ and $[M + (M + H)]^+$ behave in a similar manner. The fragmentation mechanism follows the

loss of HNO_2 in the first step, followed by the loss of NO_2 , or O and NO, additional loss of NO, and finally, the loss of CO leading to rupture of cage structure as depicted in Figure 2.

4. Summary

A general scheme for the formation of diagnostic ions for molecular weight assignment and a general fragmentation mechanism for polynitrocage compounds have been described. These schemes have enabled us to identify or confirm numerous new synthetic intermediates.

5. Reference

1. T. H. Chen and C. Campbell, Proceedings of the Third International Symposium on Analysis and Detection of Explosives, July 10-July 13, 1989, Mannheim-Neuostheim, Federal Republic of Germany, pp. 26-1 to 26-24.

PREDICTION OF THE LIFE-TIME OF NYLON 6/6 EXPOSED TO JA-2 PROPELLANT

C. CAMPBELL AND T. H. CHEN

U. S. Army Armament Research, Development, and Engineering Center, Picatinny Arsenal, New Jersey 07806-5000, U. S. A.

ABSTRACT. As part of the efforts to predict the compatibility of energetic materials and other materials, a rapid predictive method has been developed for determining the compatibility of Nylon 6/6 with JA-2 propellant. The method is based on the correlation of the decrease of the crystallinity of Nylon 6/6, when exposed to JA-2, with the exposure time and temperature using differential scanning calorimetry. An equation was then derived to predict the life-time of Nylon 6/6 exposed to JA-2 as a function of time and temperature. This paper will briefly describe the method developed and discussed the results obtained.

1. Introduction

The current practice of determining the life-time of plastic components which are employed in the ammunitions is time-consuming and costly to the development of a new ammunition system. Typically, one to two years is required to assess the effects of propellant vapors on the plastic components at 60 °C. It is highly desirable, therefore, to have a rapid method of screening the potential plastic components as well as to determine the life-time of the candidate plastics in the ammunition. The objective of this paper is to develop such method.

2. Experimental

2.1. APPARATUS

The Perkin-Elmer DSC-4 differential scanning calorimeter (DSC) system and the Beckman FT1100 Fourier transform infrared spectrophotometer (FTIR) were used in the isothermal and temperature programmed DSC and FTIR studies, respectively. High pressure gold-plated stainless steel sample holders were used in all DSC experiments.

3. Results and Discussion

The method is based on the correlation of the decrease of the crystallinity of Nylon 6/6, when exposed to JA-2, with the exposure time and temperature using differential scanning calorimetry. An equation was then derived to predict the life-time of Nylon 6/6 exposed to JA-2 as a function of time and temperature. Further, FTIR was used to elucidate the cause of Nylon 6/6 deterioration.

3.1. KINETICS

Fine shavings of Nylon 6/6 specimens were mixed with JA-2 (1 : 1 ratio) and heated isothermally at 140, 150, 160, 170, and 180 °C for a fixed period of time of up to about 200 minutes to obtain kinetic data. After heating, the sample container was opened and the heated specimen was removed and extracted with acetone to remove JA-2. The residue was then dried and a temperature programmed DSC run made at 10 °C/min. to 320 °C. The logarithms of the heat of fusions obtained as a function of temperature and time were plotted vs. time to examine the order of the reaction.

Figure 1 shows this plot. Thus, the decrease in the heat of fusion follows the first order kinetics quite well (Equation 1).

$$\ln (C/C_0) = - kt \quad (1)$$

where C and C₀ are the degrees of crystallinity at time t and 0, respectively and k is the reaction constant. The latter is then plotted vs. the reciprocal of absolute temperature (1/T) to obtain the activation energy (Figure 2). This results in Equation (2).

$$k = 4.39 \times 10^{11} e^{(-27,300 \pm 700)/RT} \quad (2)$$

k in min⁻¹; Ea in cal/mole

This equation predicts a value of 0.57 ± 0.25 for C/C₀ at 60 °C and t = 24 months which agrees quite well with that obtained based on compressive strength measurement of tensile bars conducted independently, i.e., 0.62 ± 0.11 .

This method should be applicable to any plastics which exhibit significant degree of crystallinity.

3.2 FTIR

Figure 3 shows the appearance of new absorption bands near 800 and 1750 cm⁻¹ which were attributed to the absorptions of primary amine and carboxyl groups. The new exothermic peak centering at about 210 °C of heated Nylon 6/6 is attributed to the hydrolysis of the polyamide chains since the kinetics of formation and decay of the new absorption bands match with those of DSC data on the new exothermic peak fairly well.

4. Conclusion

A rapid method for the determination of the life-time of Nylon 6/6 components in contact with JA-2 propellant in ammunitions has been developed. The predicted life-time for Nylon 6/6 in

contact with JA-2 was shown to be in good agreement with that obtained from compressive strength measurement at 60 °C after an aging period of 24 months. The new feature observed in the DSC studies was attributed to the hydrolysis of polyamide chains based on FTIR studies and correlation of DSC and FTIR data.

This method should be applicable to any plastics which exhibit significant degree of crystallinity.

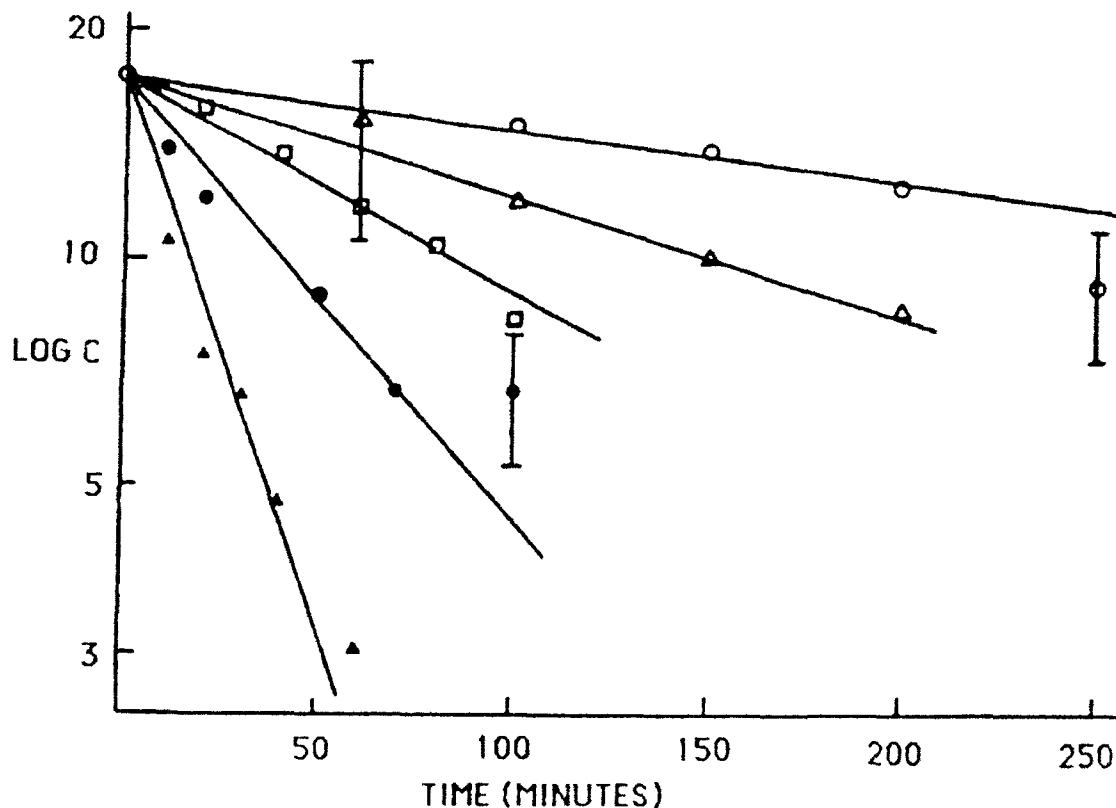
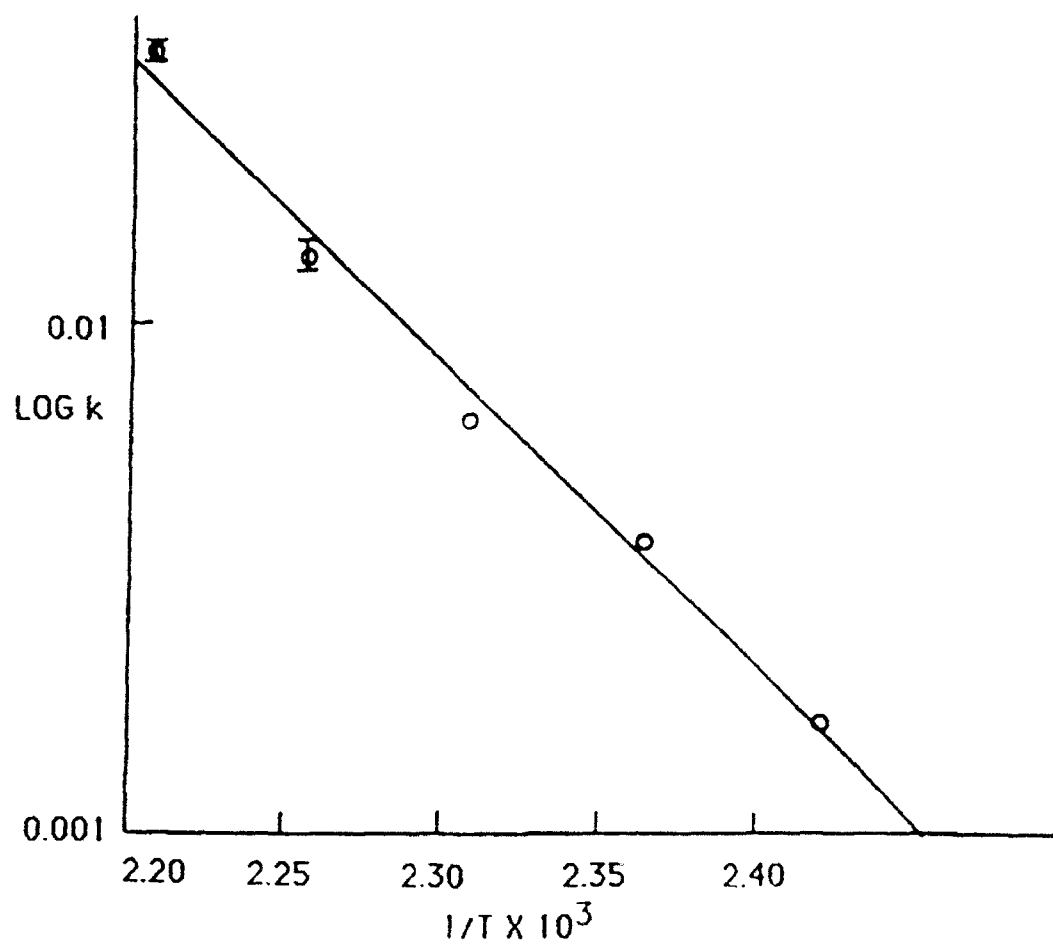


FIGURE 1. LOG C VS t PLOT
 OPEN CIRCLE, 140 °C; OPEN TRIANGLE, 150 °C; OPEN
 SQUARE, 160 °C; SOLID CIRCLE, 170 °C; SOLID TRIANGLE,
 180 °C

FIGURE 2. LOG k VS $1/T$ PLOT

101 [DISK1] 4 cm-1 25180/20 [DISK1] 4 c

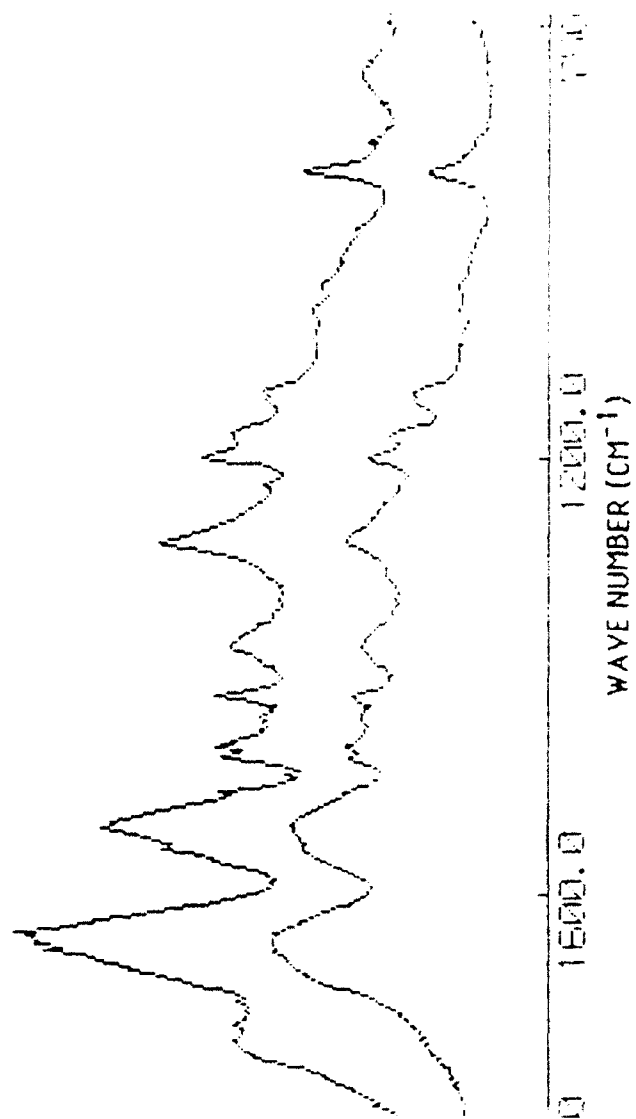


FIGURE 3. FTIR SPECTRA OF ZYTEL 101
TOP, HEATED WITH JA-2 FOR 20 MIN AT 180 °C; BOTTOM,
CONTROL

MS/MS CID FRAGMENTATION PROCESSES IN NITRONAPHTHALENES

J. YINON

Department of Environmental Sciences and Energy Research
Weizmann Institute of Science
Rehovot 76100
Israel

ABSTRACT. Mass spectral fragmentation processes and pathways of a series of nitro, dinitro and trinitro derivatives of naphthalene have been studied. Collision induced dissociation (CID) mass spectra were obtained using a tandem BB mass spectrometer (MS/MS). Major fragmentation pathways included loss of NO_2 from the molecular ion, followed by loss of NO and/or CO. Additional fragmentations included loss of OH from the molecular ion in some of the investigated compounds.

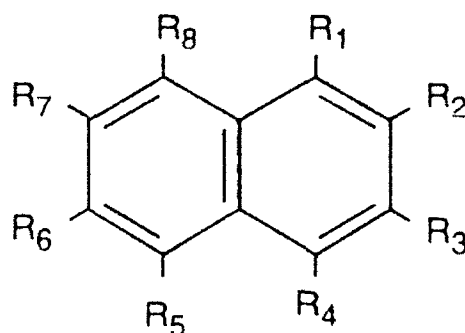
1. Introduction

Until the end of World War I, nitro derivatives of naphthalene were widely used in mixtures with other explosives, such as picric acid and ammonium nitrate [1].

At present, nitronaphthalenes are not used in the manufacture of explosives, mainly because of the shortage of naphthalene, which is widely used in the manufacture of phthalic acid and dye intermediates.

Nitronaphthalene is not an explosive. Dinitronaphthalene shows weak explosive properties, and only trinitronaphthalene may be considered as an explosive. Tetranitronaphthalene is as powerful an explosive as TNT [1]. The advantage of nitronaphthalenes is that they are only slightly toxic, as opposed to the high toxicity of TNT. Because of the environmental toxic effects of TNT [2], a renewed interest in the nitronaphthalenes has developed.

In order to contribute to the understanding of these compounds we have studied the mass spectral fragmentation processes and pathways of a series of nitro, dinitro and trinitro derivatives of naphthalene (1-7)



No.	Compound	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	R ₈
1	1-Nitronaphthalene	NO ₂	H	H	H	H	H	H	H
2	1,3-Dinitronaphthalene	NO ₂	H	NO ₂	H	H	H	H	H
3	1,8-Dinitronaphthalene	NO ₂	H	H	H	H	H	H	NO ₂
4	1,5-Dinitronaphthalene	NO ₂	H	H	H	NO ₂	H	H	H
5	2,7-Dinitronaphthalene	H	NO ₂	H	H	H	H	NO ₂	H
6	1,3,8-Trinitronaphthalene	NO ₂	H	NO ₂	H	H	H	H	NO ₂
7	1,4,5-Trinitronaphthalene	NO ₂	H	H	NO ₂	NO ₂	H	H	H

2. Experimental

The instrument used was a tandem mass spectrometer consisting of two magnetic sector analysers with a collision cell located in the region between them. A full description of the instrument has been reported elsewhere [3]. Argon was used as collision gas and its pressure was measured with an ion gauge in the housing of the cell. The pressure of the argon was adjusted so that the precursor ion beam intensity was reduced to half of its initial value. The ion gauge then showed an increase in pressure from 1×10^{-7} to 5×10^{-6} Torr.

Compound 1 was purchased from Eastman Kodak (Rochester, NY, USA), compounds 2 and 3 from Aldrich Chemical (Milwaukee, WI, USA), compounds 4 and 5 from Fluka Chemie (Buchs, Switzerland) and compounds 6 and 7 from Pfaltz & Bauer (Flushing, NY, USA).

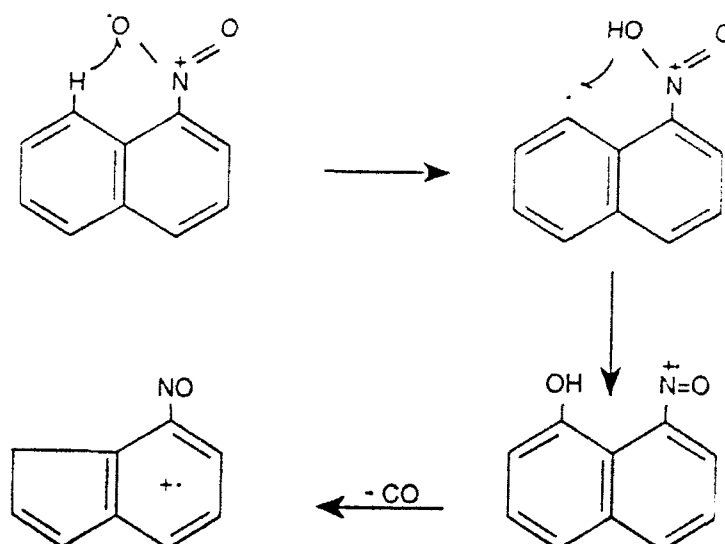
Samples were introduced through the solids probe. The ionization mode was EI at 70 eV. The ion source was operated at 150-250°C.

3. Results and Discussion

3.1. 1-NITRONAPHTHALENE

In 1-nitronaphthalene no loss of CO from the molecular ion was observed, although it had been suggested as an EI fragmentation by Beynon et al. [4] and later on by Djerassi's group [5]. Instead, loss of NO was found to be a major fragmentation. Therefore, the CID mass spectrum was recorded also at low energies, on a triple quadrupole MS/MS [6]. Loss of CO was observed at a collision energy of 20 eV, but at energies of 50 eV and higher, no such loss was observed, but mainly loss of NO.

Beynon et al. [4] proposed the following mechanism for the loss of CO.



It was proposed that loss of CO occurred through attack of oxygen on the C-8 atom, which is located near the nitro group. This thesis was supported by the observation [4] that 1-nitronaphthalene bearing an 8-substituent (NH_2 or NO_2) did not eliminate CO. Loss of CO in the low energy CID (but not in high-energy CID) supports the proposed mechanism which includes a rearrangement process.

3.2. DINITRONAPHTHALENES

Figures 1 to 4 show examples of CID mass spectra of some of the dinitronaphthalenes.

Figures 1 and 2 represent the CID mass spectra of the molecular ion and of the $(\text{M}-\text{OH})^+$ ion of 1,3-dinitronaphthalene, respectively.

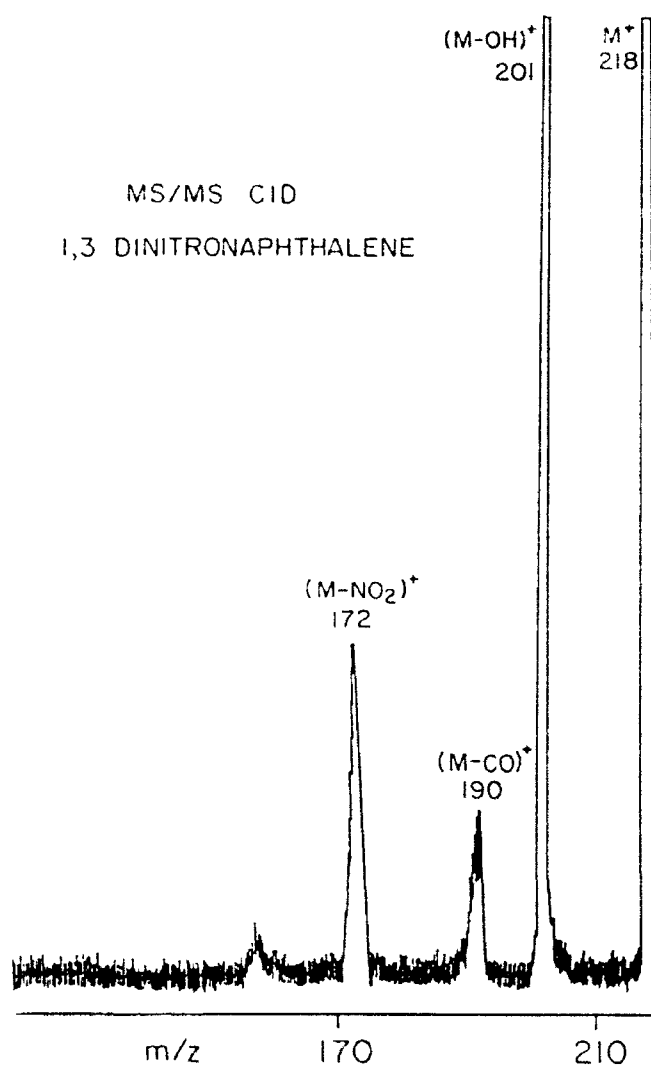


Figure 1. CID mass spectrum of M⁺ of 1,3-dinitronaphthalene

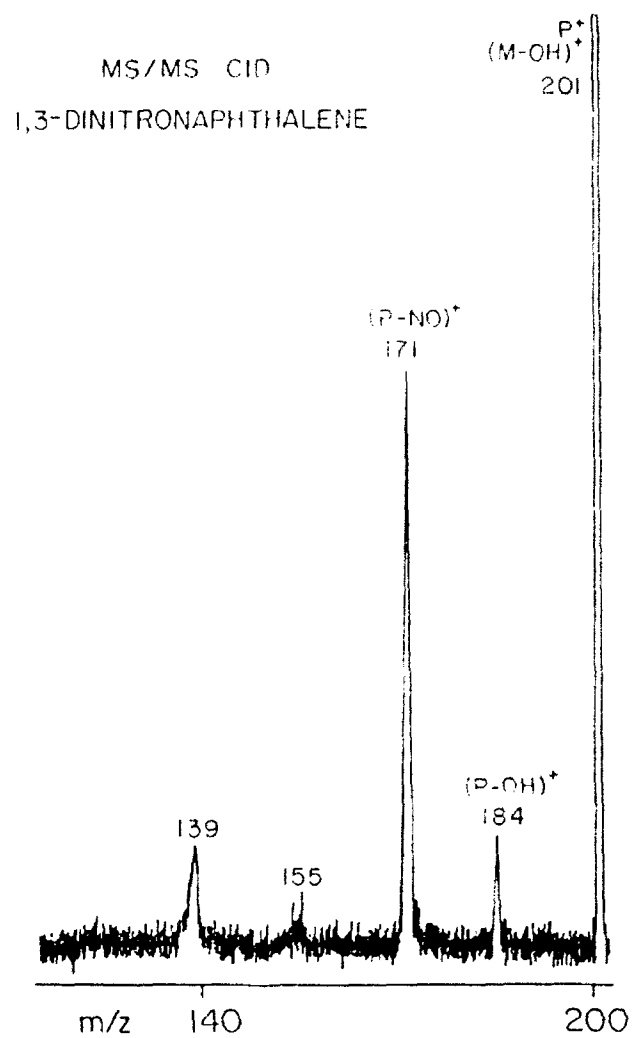


Figure 2. CID mass spectrum of $(M-OH)^+$ of 1,3-dinitronaphthalene

Figure 3 shows the CID spectrum of the molecular ion of 2,7-dinitronaphthalene, and Figure 4 the CID spectrum of the $(M-NO_2)^+$ ion of 1,8-dinitronaphthalene.

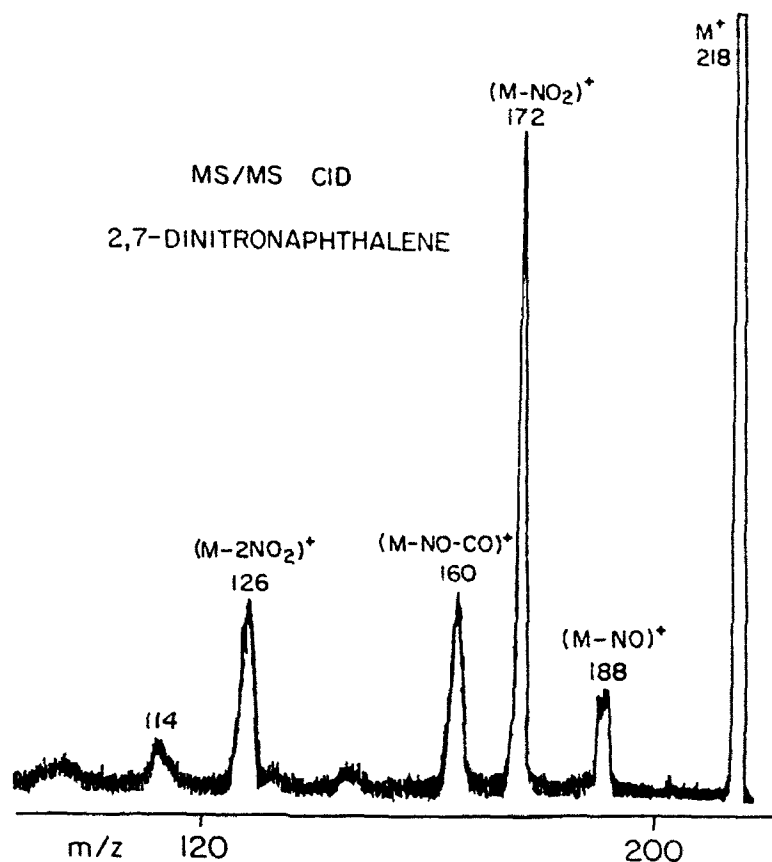


Figure 3. CID mass spectrum of M^+ of 2,7-dinitronaphthalene

The major fragmentations in dinitronaphthalenes were loss of NO_2 , NO , $(NO+CO)$ and $2NO_2$. Loss of CO from the molecular ion was found to be a minor fragmentation, and occurred only in 1,3-dinitronaphthalene (Figure 1). However, loss of CO was observed to occur from the $(M-NO)^+$ and $(M-NO_2)^+$ fragment ions. Figure 5 shows a proposed CID fragmentation map of dinitronaphthalenes.

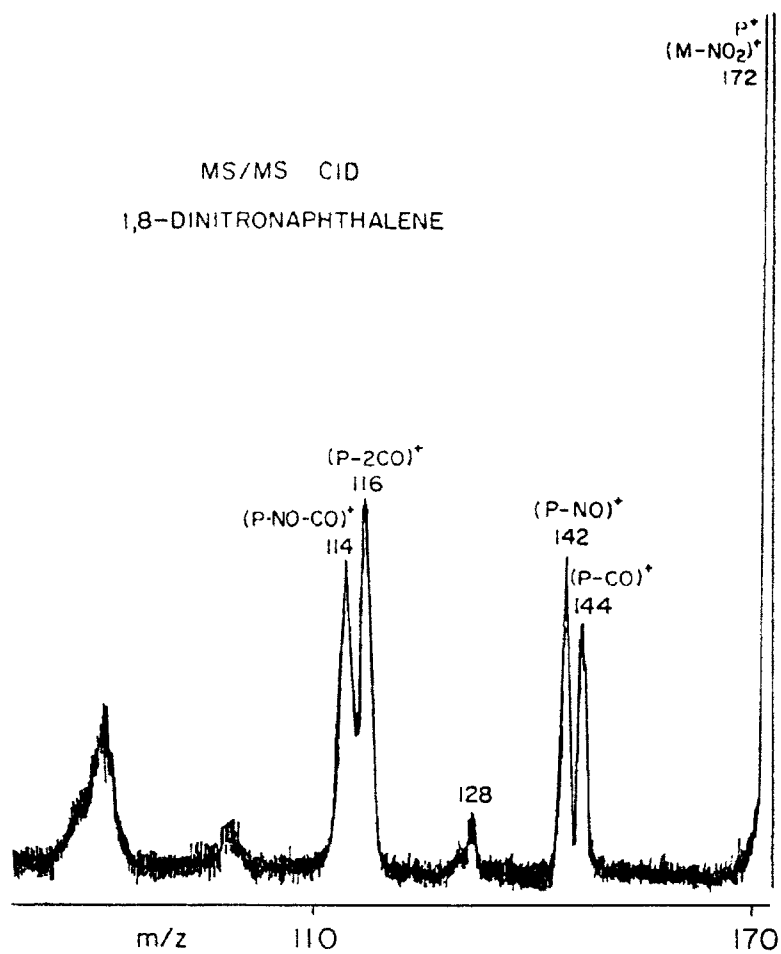


Figure 4. CID mass spectrum of $(M-NO_2)^+$ of 1,8-dinitronaphthalene

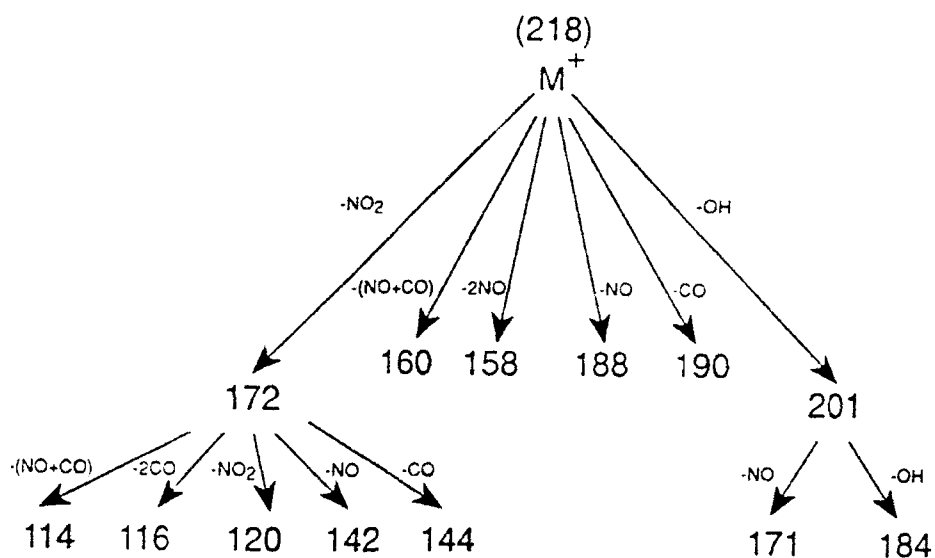


Figure 5. CID fragmentation map of dinitronaphthalenes

3.3. TRINITRONAPHTHALENES

The trinitronaphthalenes did not lose any CO from their molecular ions, although loss of CO was observed to occur from the $(M-NO_2)^+$ and $(M-NO_2-NO)^+$ fragment ions.

Figures 6 and 7 show the CID mass spectra of the molecular ion and of the $(M-NO_2)^+$ ion of 1,4,5-trinitronaphthalene

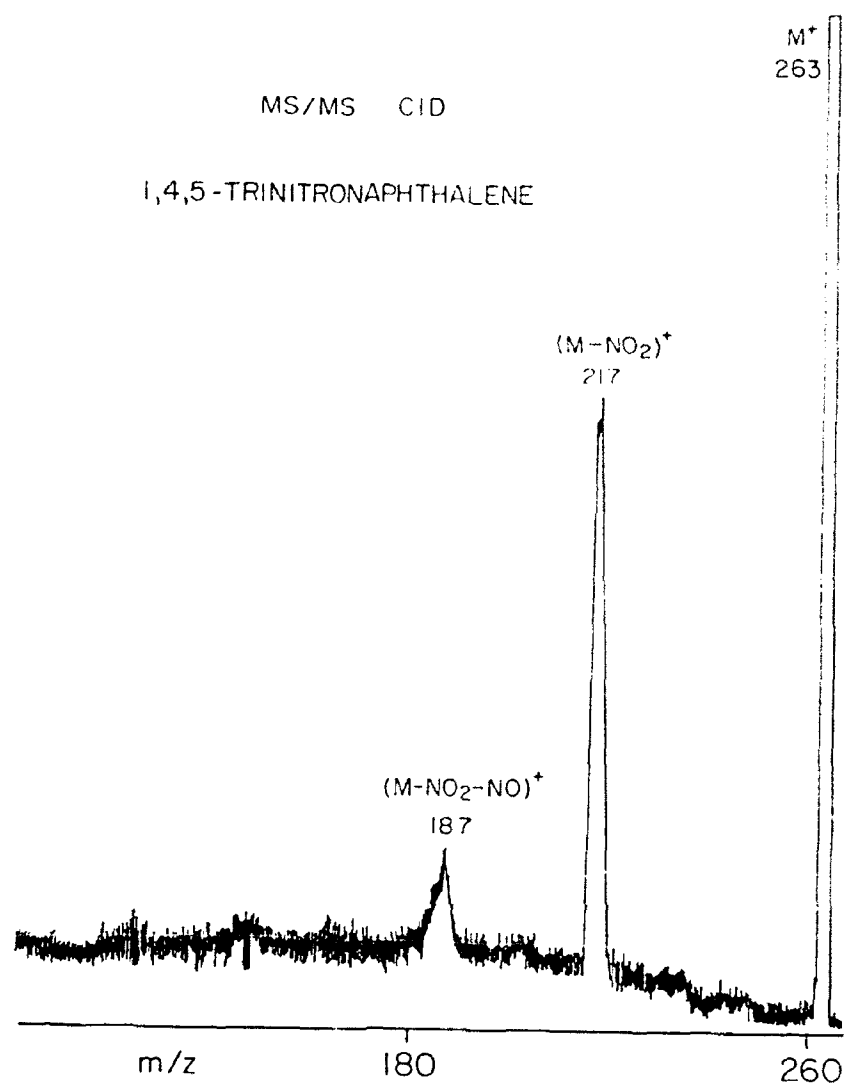


Figure 6. CID mass spectrum of M^+ of 1,4,5-trinitronaphthalene

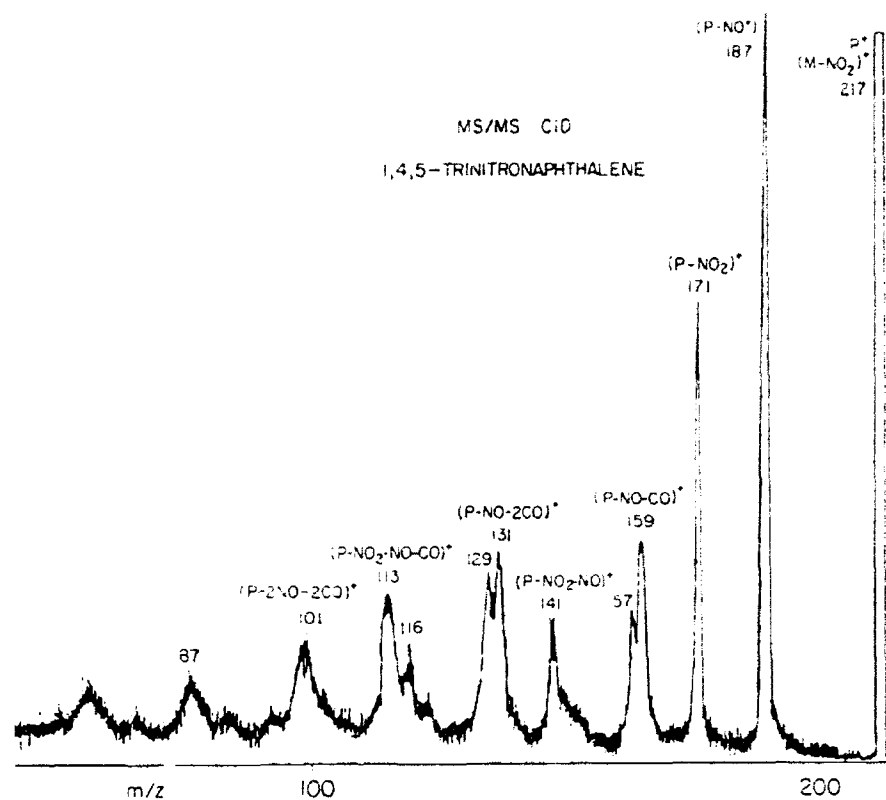


Figure 7. CID mass spectrum $(M-NO_2)^+$ of 1,4,5-trinitronaphthalene

Figures 8 and 9 show the CID mass spectra of the molecular ion and of the $(M-NO_2-NO)^+$ ion of 1,3,8- trinitronaphthalene.

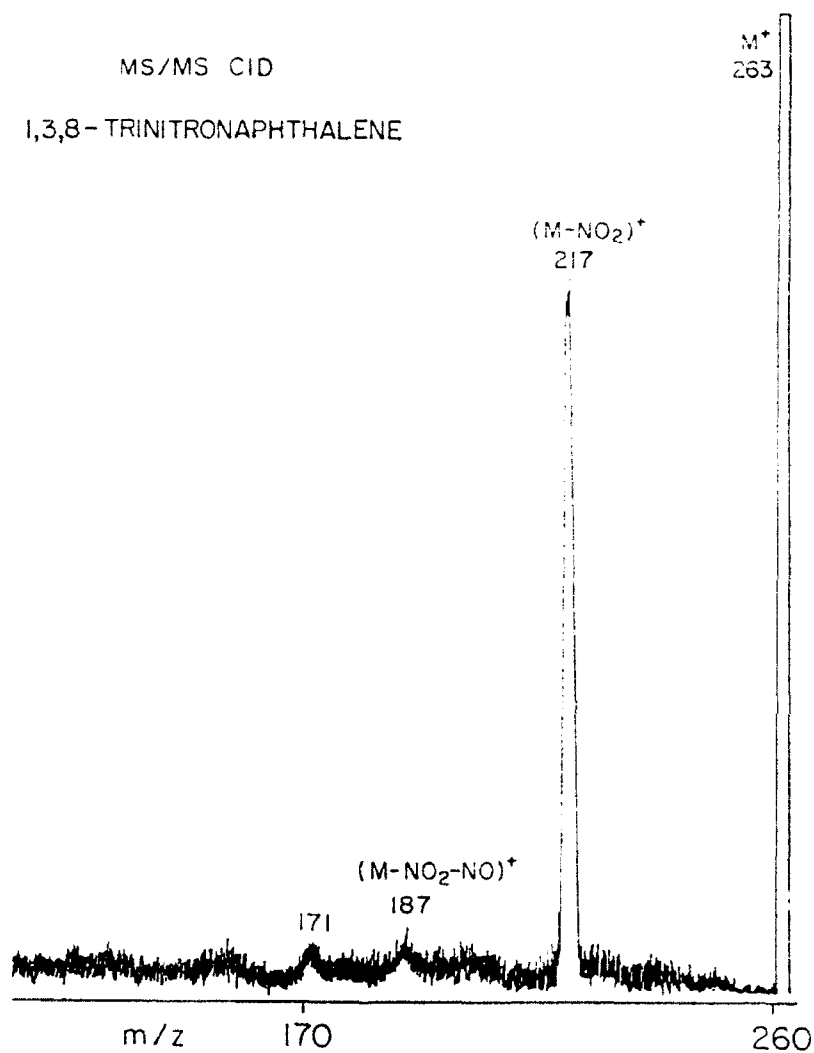


Figure 8. CID mass spectrum of M^+ of 1,3,8-trinitronaphthalene

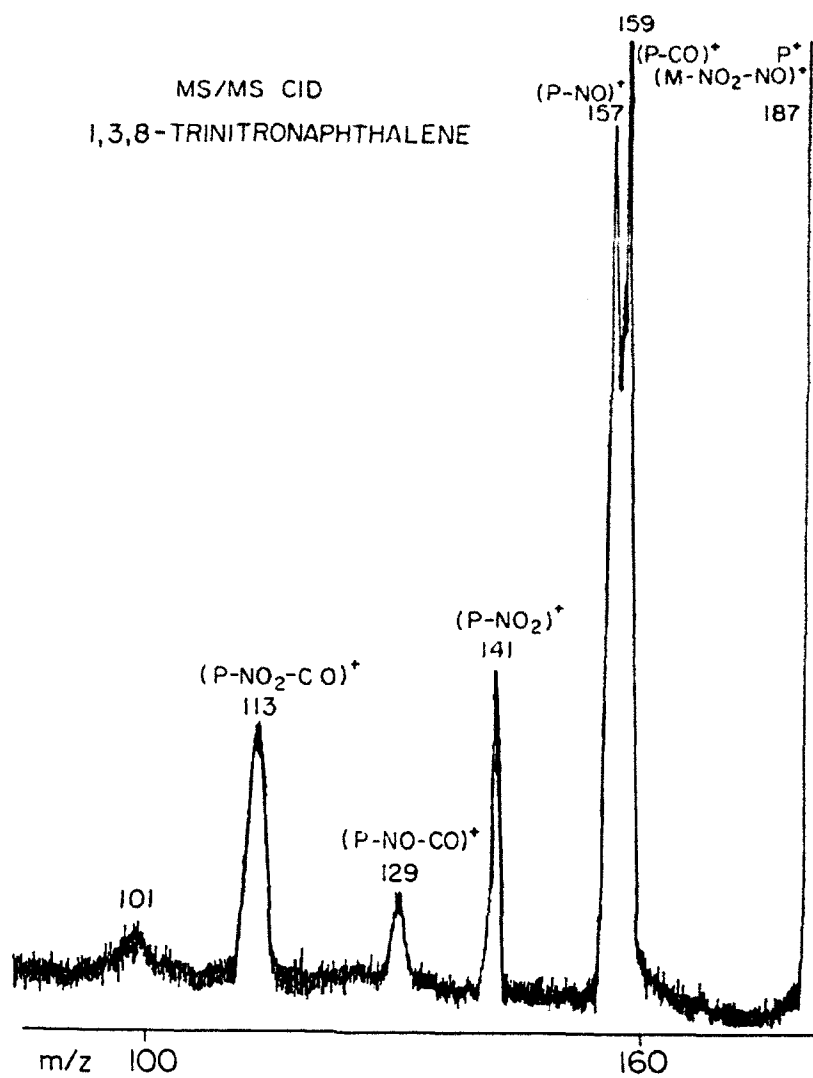


Figure 9. CID mass spectrum of $(M-NO_2-NO)^+$ of 1,3,8-trinitronaphthalene

Figure 10 shows a proposed fragmentation map of trinitronaphthalenes.

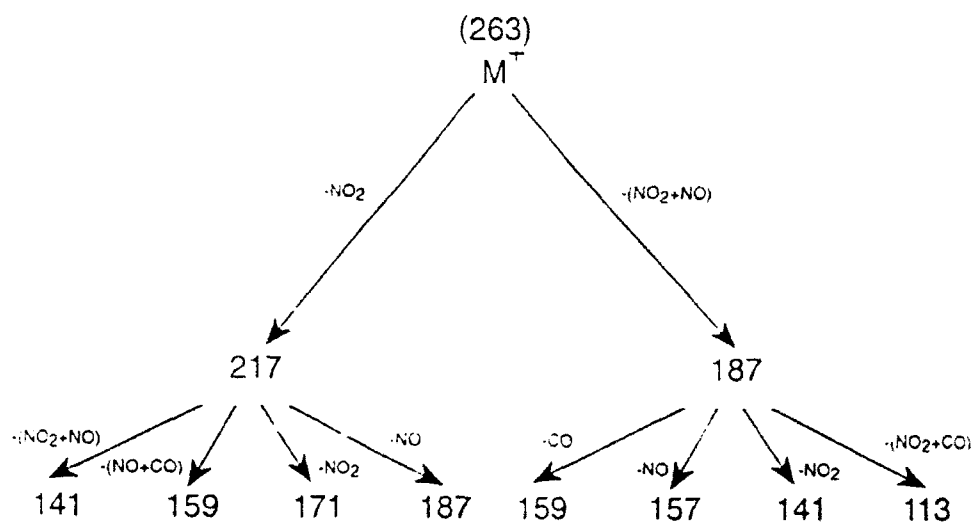


Figure 10. CID fragmentation map of trinitronaphthalenes

4. Conclusions

These preliminary results show that loss of CO from 1-nitronaphthalene is energy-dependent, as this loss involves a rearrangement process. As the number of nitro groups on the naphthalene structure increases, loss of CO becomes less probable, which indicates a higher stability of the molecule.

Additional studies on the energy-dependence of the CID of nitronaphthalenes are planned.

ACKNOWLEDGEMENT

The author gratefully acknowledges Dr. L.D. Betowski, EPA Environmental Monitoring Systems Laboratory, Las Vegas, NV, for the low-energy CID measurement of 1-nitronaphthalene.

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TANDEM MASS SPECTROMETRIC IDENTIFICATION OF EXPLOSIVES ADSORBED ON ORGANIC SUBSTRATES.

A.D. Wright and K.R. Jennings
Department of Chemistry
University of Warwick
COVENTRY
CV4 7AL, U.K.

and R. Peters
DRA
RARDE Fort Halstead
SEVENOAKS
TN14 7BP, U.K.

ABSTRACT. Both electron and chemical ionisation coupled with collision-induced dissociation mass spectrometry can be used for the detection of energetic materials adsorbed on organic substrates without the need for sample preparation. For 2,4,6-trinitrotoluene in particular, this method is sufficiently sensitive to detect 0.9ng of explosive adsorbed on a small strip car seat material.

1. INTRODUCTION

The persistence of explosives on organic materials is of great interest to the forensic scientist. It is well known that the volatile components of propellants and explosives are adsorbed on or absorbed by the skin and clothing of a person using a firearm[1] and that the components of plastic explosives are also transferred to the skin on contact and can remain detectable on skin for several days after initial exposure[2]. Mass spectrometry is generally used for the detection of such residues in association with some form of chromatographic separation, i.e. gcms. Tandem mass spectrometry has mainly been limited to studies of pure explosives in which the product ion spectra have been recorded of several different explosives[3-8].

We present the results of a study of the product ion mass spectra of protonated molecule ions generated by isobutane chemical ionisation of cyclomethylene trinitramine (RDX) and pentaerythrityl tetranitrate (PETN) and product ion spectra of abundant fragment ions formed by electron ionisation of 2,4,6-trinitrotoluene (TNT). Spectra were obtained from both pure explosives and explosives adsorbed on organic substrates such as human hair and man-made fibres.

In order to ascertain whether a particular explosive is present in a sample, the collision-induced dissociation (CID) mass spectrum of the sample is recorded. The presence or absence of the peaks characteristic of the explosive is used to indicate the presence or absence of the explosive in question. Interference from isobaric ions is more likely to occur at lower masses, therefore, selection of ions of high mass in the mass spectrum will allow one to use the minimum resolving power for selection of the precursor ions and therefore gain maximum sensitivity. Chemical ionisation was selected as the ionisation method of choice since it is a 'soft' ionisation method; the production of abundant MH^+ ions should allow for a sensitive analysis of

contaminated materials. Experiments can however be performed using electron ionisation. CID of abundant fragment ions generated by electron ionisation can also be used to indicate the presence of explosives adsorbed on the same substrates.

2. EXPERIMENTAL

2.1. MASS SPECTRA

All mass spectra were recorded using a Kratos Analytical Concept II HH four-sector mass spectrometer operating at an accelerating voltage of 8kV. The electron energies used for electron and chemical ionisation were 70eV(100mA) and 100eV(500mA), respectively. For chemical ionisation, isobutane was used as the reagent gas at a pressure of 10^{-5} Torr as indicated by an ionisation gauge in the source housing. In all experiments, the ion source temperature was maintained at 150°C.

CID mass spectra of ions selected using the first mass analyser were recorded by means of a linked-scan[9] of the second magnetic and electrostatic fields. The collision gas, helium, was admitted to the collision cell until the precursor ion beam was attenuated by 40-50%. The collision cell was electrically floated to 4kV. The resolving power for the primary separation was generally in excess of 3000; for the second mass analyser a resolving power of approximately 1000 was used.

2.2. PREPARATION OF SAMPLES

Small samples of hair, car seat lining, car door lining and polyester-cotton material were soaked in 10^{-5} mol dm⁻³ solutions of explosive materials in acetone for a period of 150 hours. Additionally, samples of these materials were doped with known amounts of TNT in 10μL aliquots of acetone.

3. Results and Discussion

3.1. CHEMICAL IONISATION AND CID MASS SPECTRA

Isobutane chemical ionisation of both RDX and PETN results in the generation of moderate abundances of MH⁺ ions. CID of the MH⁺ ions, m/z 223, generated by chemical ionisation of RDX results in a simple spectrum containing ions at m/z 149, 105 and 75 (Figure 1a). CID mass spectra of the materials doped with RDX were recorded under the same conditions and are also shown in Figures 1b-1d. These spectra, with one exception, resemble closely that of the spectrum of pure RDX. In the CID spectrum of the contaminated car seat lining (Figure 1d), however, there is a great deal of chemical background resulting from CID of ions of m/z 223 formed from the substrate itself. These interferences can be removed by operating the first mass analyser at even higher resolving power, but only at the expense of sensitivity. The chemical ionisation mass spectrum of the hair sample which has been treated with RDX is shown in Figure 2. This spectrum, in which it is not possible to see any ions resulting from RDX shows clearly the advantage of using tandem mass spectrometry to this type of problem.

CID of MH⁺ ions, m/z 317, formed from PETN also produces a simple mass spectrum. Only ions at m/z 76, 46 and 30 are formed with reasonable abundance (Figure 3a). The CID spectra of

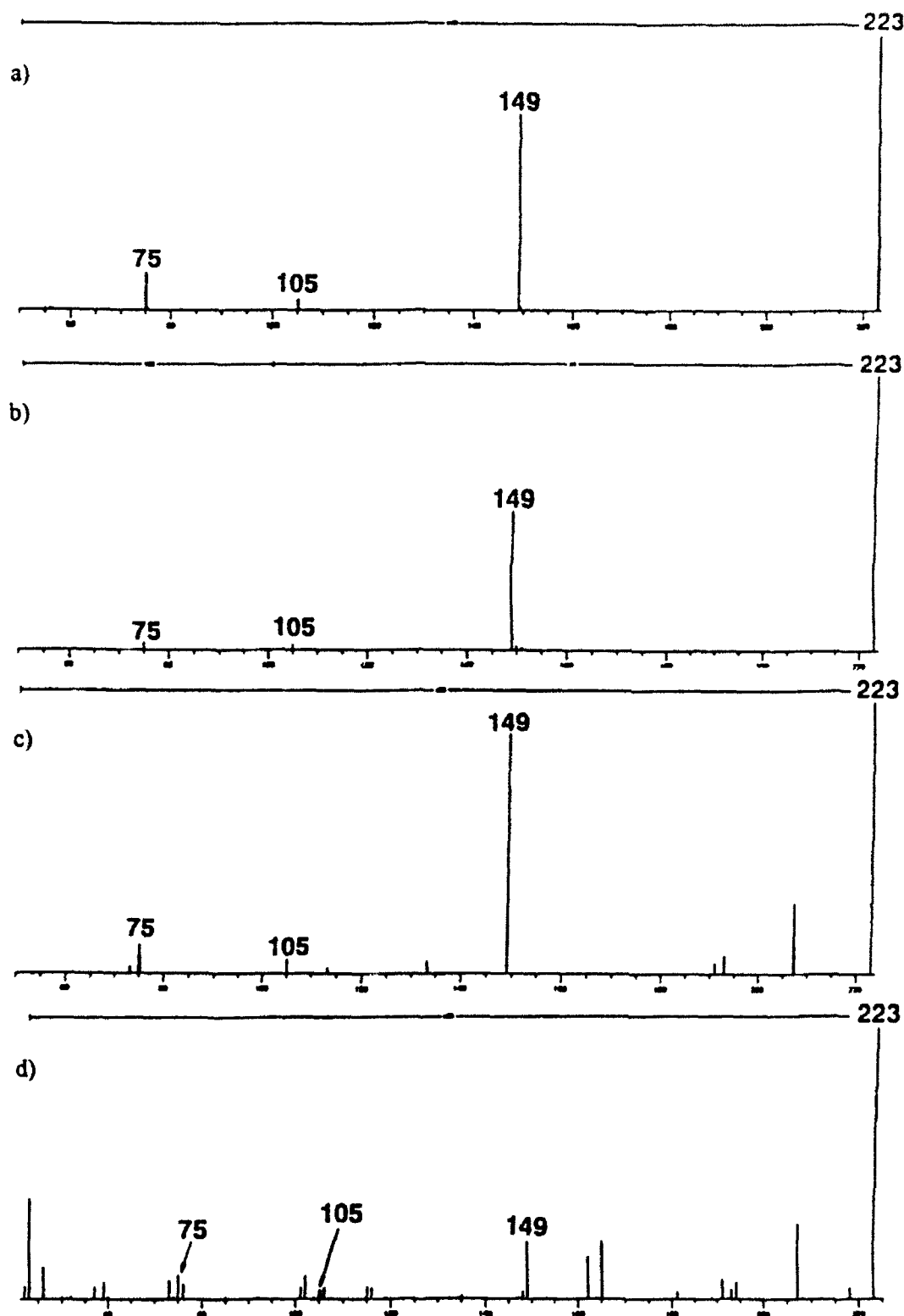


Figure 1. CID mass spectra of m/z 223 from chemical ionisation of a) RDX, b) polyester-cotton material + RDX, c) hair + RDX and d) car seat lining + RDX.

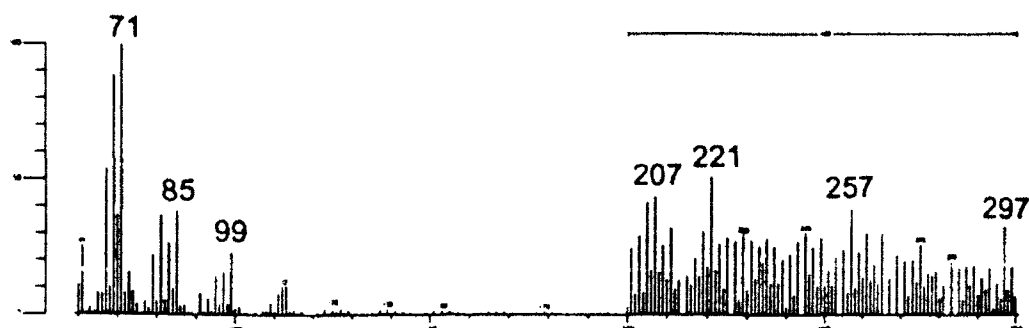


Figure 2. CI mass spectrum of hair treated with RDX.

the substrates doped with PETN are presented in Figures 3b-3d. Again, these spectra resemble the spectrum of the pure explosive with the exception of the car seat lining. Similarly, this spectrum contains peaks due to fragment ions formed from ions of m/z 317 formed from the substrate itself.

3.2. ELECTRON IONISATION AND CID MASS SPECTRA

Electron ionisation of RDX does not produce intact molecular ions, M^+ . However, an abundant fragment ion, m/z 128, is formed. CID of this ion produces a spectrum containing ions which can be considered to be characteristic of the structure of this fragment ion (Figure 4a). CID mass spectra of the contaminated substrates (Figures 4b-4d) reveal clearly the presence of RDX in each sample. Problems caused by interferences are minimal in this particular case.

Electron ionisation of TNT produces only a low abundance of M^+ ions but the fragment ion formed by loss of $OH\cdot$, m/z 210, is the base peak in the mass spectrum. CID of this highly abundant ion produces the spectrum shown in Figure 5a. Figures 5b-5d show the spectra obtained from the car seat lining doped with 900, 9 and 0.9ng TNT, respectively. The sample containing 0.9ng TNT produced a spectrum containing all of the peaks associated with TNT and very low intensity peaks due to fragment ions formed from m/z 210 from the substrate.

4. Conclusions

Both RDX and PETN can be detected by collision induced dissociation mass spectrometry of MH^+ ions formed by isobutane chemical ionisation. The spectra resulting from CID are relatively simple which enables the rapid identification of the presence of these materials on complex matrices.

Electron ionisation of RDX and TNT, followed by CID of abundant fragment ions, also allows one to detect these materials adsorbed on organic substrates. In the case of TNT, excellent spectra can be obtained from 0.9ng TNT on thin strips of the substrates examined.

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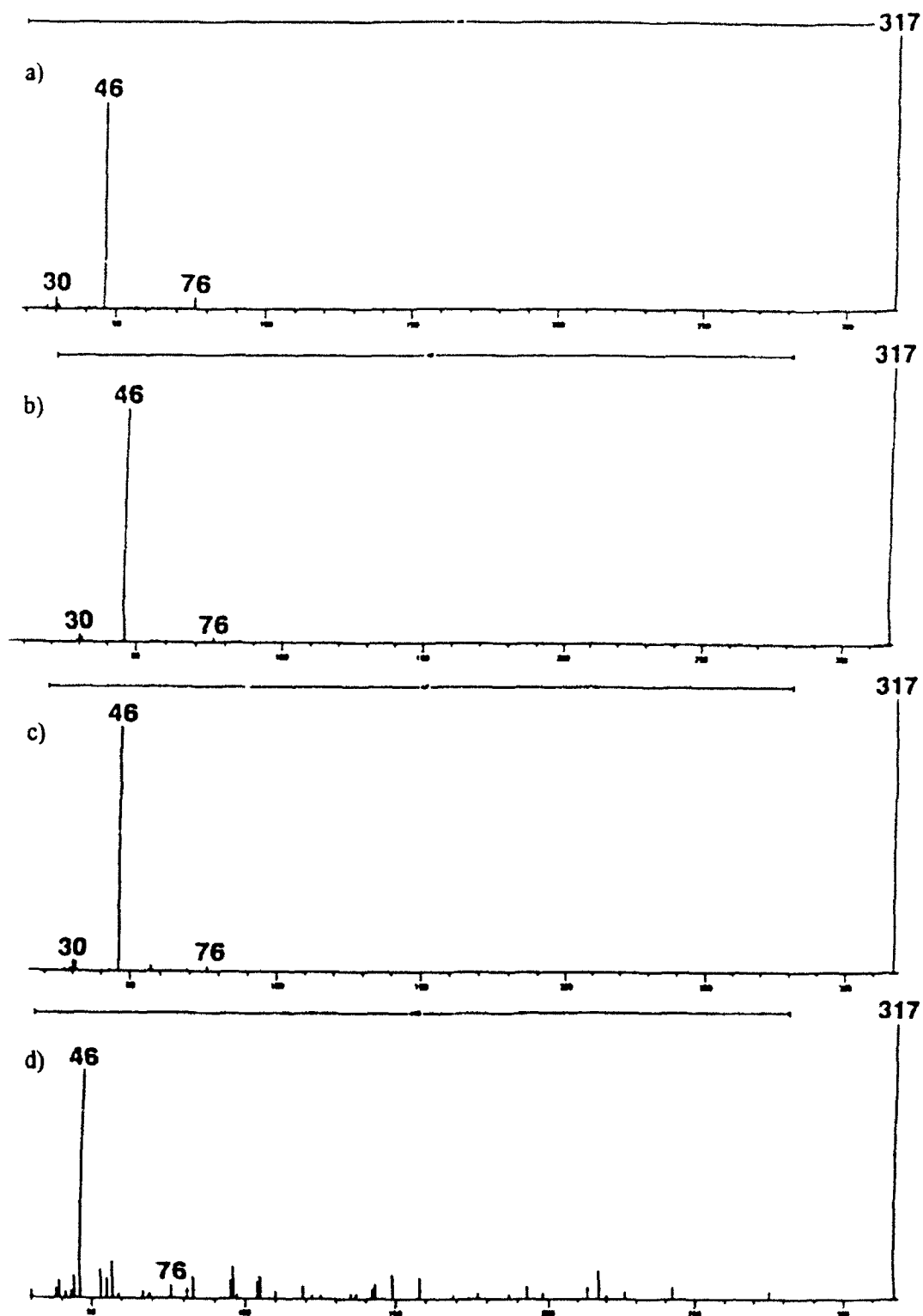


Figure 3. CID mass spectra of m/z 317 from chemical ionisation of a) PETN, b) polyester-cotton material + PETN, c) hair + PETN and d) car seat lining + PETN.

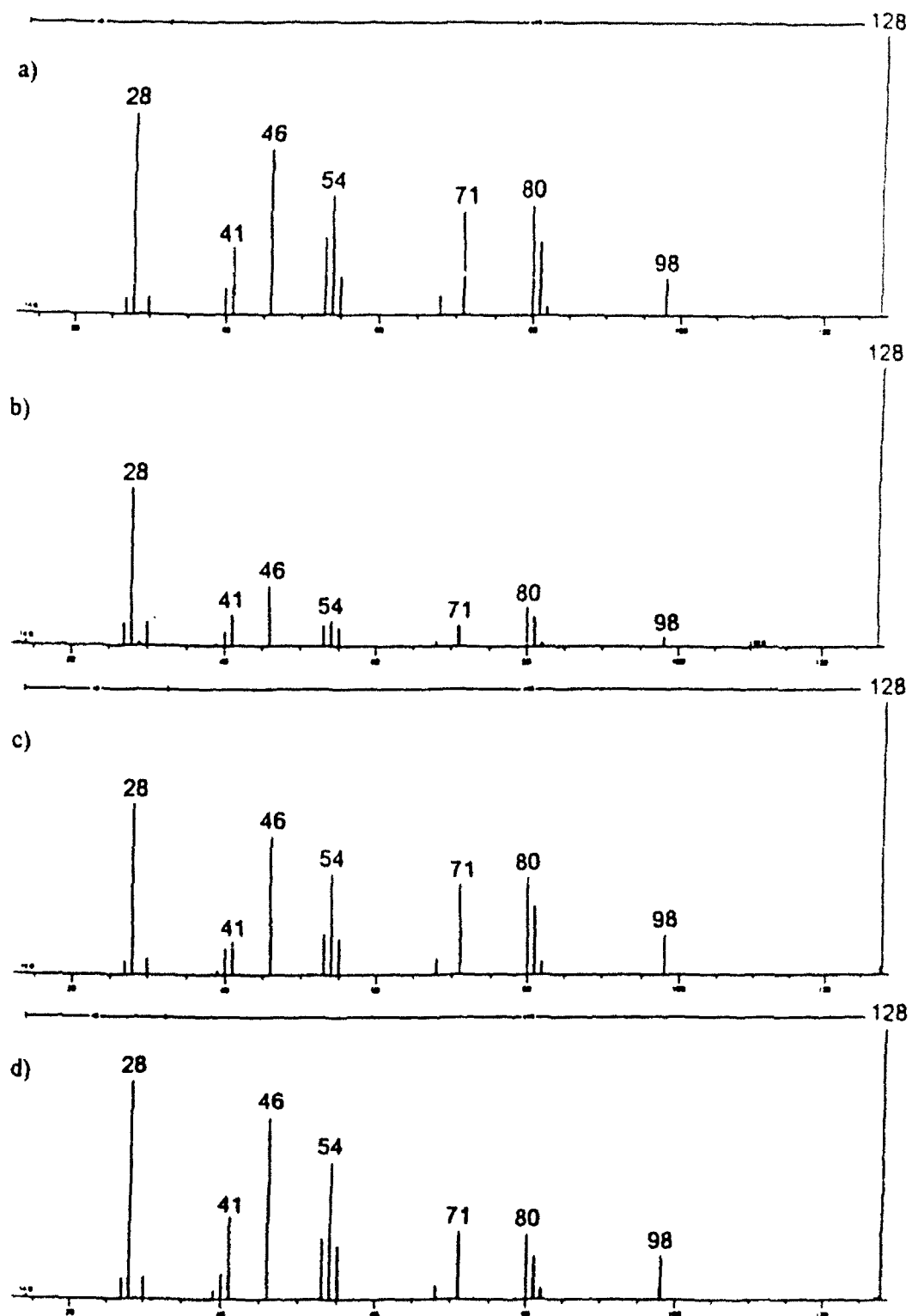


Figure 4. CID mass spectra of m/z 128 from electron ionisation of a) RDX, b) car door lining + RDX, c) polyester-cotton material + RDX and d) hair + RDX.

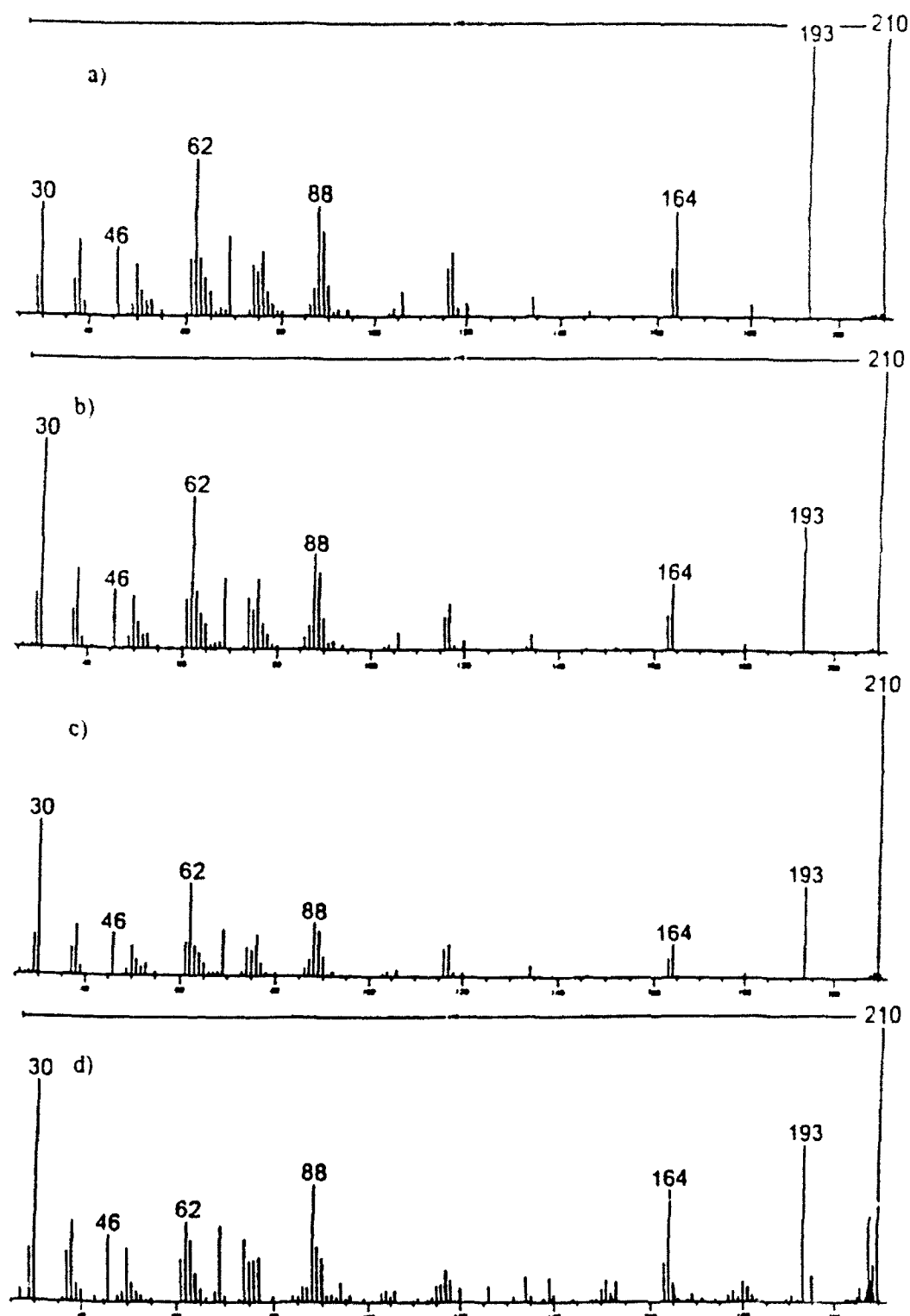


Figure 5. CID mass spectra of m/z 210 from electron ionisation of a) TNT, b) car door lining + 900 ng TNT, c) car door lining + 9 ng TNT and d) car door lining + 0.9 ng TNT.

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ADDUCT IONS IN MASS SPECTROMETRY OF NITRAMINE MUNITIONS COMPOUNDS

ELIZABETH P. BURROWS

U.S. Army Biomedical Research and Development Laboratory
Fort Detrick, Frederick, MD 21702-5010
U.S.A.

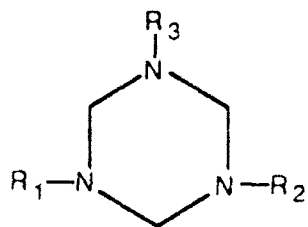
ABSTRACT. High pressure positive chemical ionization (PCI) mass spectrometry of nitramines and related compounds with a polar reagent gas, dimethyl ether, revealed that adduct ions resulting from ion-molecule reactions with reagent gas-derived ions were by far the predominant species. The m/z values of these adducts are uniquely characteristic for a particular nitramine and may be of value, either alone or in addition to molecular ion and fragment-molecule adduct ion data from methane PCI spectra, in making positive identifications of individual compounds in complex mixtures.

1. Introduction

Fragment-molecule adduct ions $[M+NO]^+$ and $[M+NO_2]^+$ were first observed in the electron ionization (EI) and positive chemical ionization (PCI) mass spectra of RDX (1a) and HMX (2a), and the respective anions were also prominent in the methane-enhanced negative chemical ionization (NCI) mass spectra of the two nitramines [1]. Collision induced dissociation (CID) experiments showed these adducts to be precursors of a majority of the fragment ions observed.

2. Instrumentation and Methods

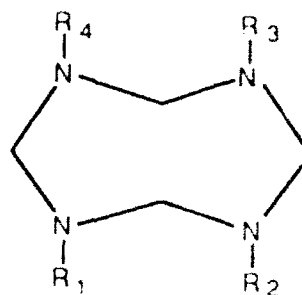
A Finnigan TSQ-70 ion source was operated at 80°C. Methane CI spectra were determined at 6 Torr; dimethyl ether (DME) CI, determined at 3 Torr, were not significantly different at 6 Torr. Use of this ion source at higher than "normal" CI source pressures has also been described by others [2]. Samples (1-5 μ g) were introduced by direct exposure desorption. CID daughters of the principal DME-derived adducts were determined with argon as collision gas at 1.2 mTorr and 20 V collision energy. Other parameters were those described previously [3,4].



1a $R_1 = R_2 = R_3 = \text{NO}_2$

1b $R_1 = R_2 = \text{NO}_2$
 $R_3 = \text{COCH}_3$

1c $R_1 = R_2 = R_3 = \text{COCH}_3$

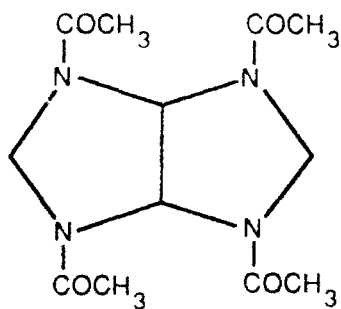


2a $R_1 = R_2 = R_3 = R_4 = \text{NO}_2$

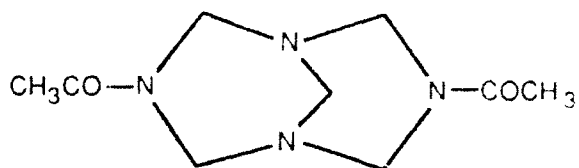
2b $R_1 = R_2 = R_3 = \text{NO}_2$
 $R_4 = \text{COCH}_3$

2c $R_1 = R_2 = R_3 = R_4 = \text{COCH}_3$

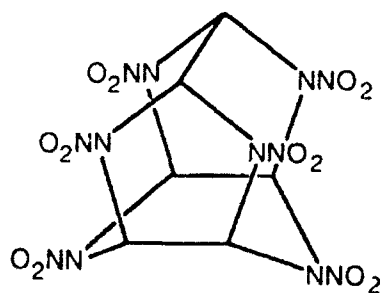
2d $R_1 = R_3 = \text{NO}_2$
 $R_2 = R_4 = \text{COCH}_3$



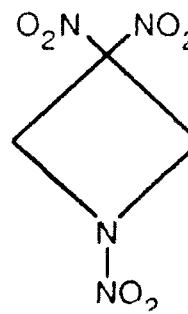
3



4



5



6

3. Results and Discussion

Recently we have examined the mass spectra of a number of related cyclic nitramines, *N*-acetylnitramines, and *N*-acetylaminines using the direct exposure probe (DEP) method of introduction [3,4]. Under these conditions in EI mode proton adducts were the most abundant, and sometimes the only, molecular ion species observed. In addition, a fragment-molecule adduct ion $[M+CH_3CO]^+$ or $[M+CH_2CO]^+$ was seen in the EI mass spectra of the monocyclic *N*-acetylaminines 1c and 2c and the bicyclic *N*-acetylaminines 3 and 4. The latter compound also displayed a higher mass fragment-molecule adduct $[M+CH_2NCOCH_3]^+$. For 1a (but not 2a) in addition to the previously reported $[M+NO]^+$ and $[M+NO_2]^+$ adducts a higher mass adduct $[M+CH_3NNO_2]^+$ was also observed.

Fragment-molecule adduct ion formation in the direct exposure PCI of 1a with isobutane as reagent gas was reported by Yinon in 1980 [5]. The predominant adduct was $[M+CH_3NNO_2]^+$, and $[M+NO]^+$ was also seen. Our observations of 1a with methane were similar, and $[M+CH_3NNO]^+$ was also present, but not $[M+NO_2]^+$. For 2a all 4 adducts were seen, with $[CH_3NNO]^+$ predominating. In general the distribution of adducts for the *N*-acetylaminines was similar in PCI to that in EI except that relative abundances were substantially greater in PCI. For *N*-acetylnitramines 1b, 2b, and 2d only proton adducts (in addition to reagent gas adducts) were observed in EI and PCI.

In NCI mode $[M+NO_2]^-$ adducts were by far the predominant molecular ion species for the nitramines and *N*-acetylnitramines, and only in the case of 1a was a trace of the lower mass adduct $[M+NO]^-$ seen. For all the *N*-acetylaminines the most abundant anion was $[M-H]^-$, and no adducts were found.

A novel polycyclic strained-cage nitramine, 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane (HNIW, 5) has recently been synthesized [6] and is under evaluation as a new solid energetic oxidizer [7]. Its high resolution EI mass spectrum has been determined and the major fragmentation processes have been documented by CID experiments [8]. The only molecular ion species observed was the proton adduct (*m/z* 439), with a relative abundance <1%. On DEP introduction of 5 we obtained a low resolution EI mass spectrum essentially identical to that published [8] except that no molecular ion species was detected. The methane PCI mass spectrum, however, showed, in addition to the proton adduct (100%) and reagent gas adducts, the fragment-molecule adducts $[M+NO]^+$ (8%) and $[M+NO_2]^+$ (2%) [9]. In NCI mode $[M-H]^-$ (100%) and $[M+NO_2]^-$ (11%) were the molecular ion species observed.

A newer and structurally simpler cyclic nitramine, 1,3,3-trinitroazetidine (TNAZ, 6), has been synthesized [10] and is under development at Picatinny Arsenal [11]. It has attracted great attention because it is sufficiently low melting as to be readily steam-castable but has an impact stability comparable to composition B and an energetic output at least 10% greater than the most powerful HMX-based formulation in use. Its EI mass spectrum was unexceptional in that the most abundant ions were fragments due to loss of NO_2 and HNO_2 , and no adducts other than the proton adduct (13%) were seen [9].

In PCI mode, however, substantial abundances of fragment-molecule adducts $[M+NO]^+$ (27%), $[M+NO_2]^+$ (14%) and $[M+HNO_2]^+$ (24%) were present in addition to the proton adduct (100%) and reagent gas adducts. For 6 in NCI by far the most abundant ion was the $[M+NO_2]^+$ adduct, and in addition two prominent adduct ions of unassigned molecular composition, $[M+99]^+$ (71%) and $[M+52]^+$ (35%), were observed.

The unusual CI reagent gas, dimethyl ether (DME), was originally reported to be useful in selective recognition of organic functional groups [12]. A recent report of DME PCI mass spectra of a number of oxo-substituted benzenes in a quadrupole ion trap mass spectrometer (ITMS) demonstrated both functional group and positional selectivity in the nature and relative abundances of reagent gas-derived adduct ions [13]. The methoxymethyl ether cation, m/z 45, induced formation of either $[M+13]^+$ or $[M+15]^+$ from each aromatic compound, depending on the functional group. ortho-Substituted bifunctional aromatics generally gave rise to $[M+13]^+$, while the meta and para isomers preferentially formed $[M+15]^+$. In a conventional triple-stage quadrupole instrument a greater abundance and variety of adducts were observed, but without the structural selectivity afforded by the ITMS [13].

These findings prompted us to examine the DME CI mass spectra of a variety of isomeric polyfunctional nitroaromatics in a conventional ion source. While isomers with two or more nitro groups only in adjacent or ortho positions (e.g. 2,3- and 3,4-dinitrotoluene) were indistinguishable in terms of the identities and relative abundances of reagent gas-derived adduct ions, other isomers displayed distributions of adduct ions which were significantly different from one another and from the ortho isomers. Thus, of the 6 trinitrotoluene (TNT) isomers, only 2,3,4- and 3,4,5-TNT were not readily distinguished by DME CI mass spectrometry [14].

We also have assessed the potential of DME as a reagent gas for uniquely and sensitively characterizing mixtures of nitramine munitions compounds and related products. Compounds 1-4 all formed at least one, and frequently two, reagent gas-derived adducts which were substantially more abundant than the proton adduct and had m/z values uniquely specific for each individual compound. The data, summarized in Table 1, show that the adducts from 1a and 2a are similar in nature and quite different from those which are predominant for all of the other heterocycles studied. Most abundant were the protonated methoxymethylene dimer adducts $[M+91]^+$; smaller amounts of methyl dimethylether adducts $[M+61]^+$ were also observed. The methoxymethylene and protonated dimethyl ether adducts $[M+45]^+$ and $[M+47]^+$ were present in little more than trace amounts.

In contrast, for *N*-acetylnitramines 1b, 2b, and 2d, and *N*-acetylaminines 1c, 2c, 3, and 4, by far the most abundant reagent adduct was $[M+45]^+$ and $[M+91]^+$ was not observed. With the exceptions of 1c and 2c, reagent adduct $[M+47]^+$ was second in abundance. Only in the cases of 4 and 5 were low abundances of methyl adducts $[M+15]^+$ also seen.

The dissociative behavior of the major adducts is summarized in

Table 2. For $[M+91]^+$, the most abundant adduct in the cases of 1a and 2a, loss of methoxymethylene (45 u) was accompanied by ring cleavage with loss of one or more CH_2NNO_2 moieties (74 u). Loss of methoxymethylene, either alone or accompanied by loss of CH_2CO (42 u) and/or $\text{CH}_2\text{NCOCH}_3$ (71 u) and/or CH_2NNO_2 , was the predominant fragmentation course for $[M+47]^+$, the second most abundant adduct in the cases of 1b, 2b, 2d, 3, and 4. The dissociation characteristics of the most abundant adducts, $[M+45]^+$, differed depending on the compound, and provided no obvious clues as to the nature of bonding in the adducts.

In conclusion, the high relative abundances of the major DME-derived adduct ions and their characteristic m/z values in the 250-400 m/z range suggest that these ionization conditions will be useful in the detection of trace amounts of individual munitions compounds in complex mixtures, and will provide information complementary to that obtained from methane PCI. Collision-induced dissociation (CID) patterns of selected ions are, of course, valuable in confirming such identifications.

4. References

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TABLE 1. Dimethyl ether PCI mass spectra of nitramines and related compounds

Cpd	principal ions m/z (% relative abundance)				
	[M+1] ⁺	[M+15] ⁺	[M+45] ⁺	[M+47] ⁺	[M+61] ⁺ [M+91] ⁺
1a	a	(0)	267 (<2)	269 (<1)	283 (43) 313 (100)
2a	b	(0)	341 (<1)	343 (6)	357 (38) 387 (100)
1b	220 (<2)	(0)	264 (100)	266 (64)	280 (6) (0)
2b	294 (4)	(0)	338 (100)	340 (70)	354 (9) (0)
2d	291 (10)	(0)	335 (100)	337 (68)	351 (12) (0)
1c	214 (36)	(0)	258 (100)	260 (12)	274 (9) (0)
2c	285 (73)	(0)	329 (100)	331 (6)	345 (9) (0)
3	283 (20)	(0)	327 (100)	329 (49)	343 (6) (0)
4	213 (25)	227 (5)	257 (100)	259 (35)	273 (3) (0)
5c	(0)	453 (5)	(0)	(0)	(0) (0)

^aThe molecular ion region featured a weak and poorly reproducible cluster; generally M⁺ (m/z 222) or [M-1]⁺ (m/z 221) predominated.

^bOnly M⁺ (m/z 296, 1%) and [M-2]⁺ (m/z 294, 2%) were observed.

^cMajor ions were M⁺ (m/z 438, 12%) and [M-NO₂]⁺ (m/z 392, 100%).

TABLE 2. CID daughter ions of principal dimethyl ether adduct ions of nitramines and related compounds^a

Cpd	Parent Adduct (PA)	Daughters
1a	313 [M+91] ⁺	194 [PA-45-74] ⁺
1b	264 [M+45] ⁺	223 [PA-41] ⁺ *191 [PA-41-42] ⁺
	266 [M+47] ⁺	*221 [PA-45] ⁺ 179 [PA-45-42] ⁺
1c	258 [M+45] ⁺	188 [PA-70] ⁺
2a	387 [M+91] ⁺	268 [PA-45-74] ⁺ *194 [PA-45-(2x74)] ⁺
2b	338 [M+45] ⁺	297 [PA-41] ⁺ 265 [PA-41-42] ⁺ 223 [PA-41-74] ⁺ *191 [PA-41-42-74] ⁺
	340 [M+47] ⁺	*295 [PA-45] ⁺ 253 [PA-45-42] ⁺ 221 [PA-45-74] ⁺ 191 [PA-45-30-74] ⁺
2c	329 [M+45] ⁺	188 [PA-70-71] ⁺

^aAsterisk denotes most abundant daughter ion.

TABLE 2. (cont) CID daughter ions of principal dimethyl ether adduct ions of nitramines and related compounds^a

Cpd	Parent Adduct (PA)	Daughters
2d	335 [M+45] ⁺	293 [PA-42] ⁺ 265 [PA-70] ⁺ 262 [PA-41-42] ⁺ *191 [PA-70-74] ⁺ 188 [PA-41-42-74] ⁺
	337 [M+47] ⁺	292 [PA-45] ⁺ 250 [PA-45-42] ⁺ *221 [PA-45-71] ⁺ 218 [PA-45-74] ⁺
3	327 [M+45] ⁺	257 [PA-70] ⁺ 254 [PA-42-41] ⁺ 213 [PA-42-71] ⁺ *183 [PA-(2x42)-60] ⁺
	229 [M+47] ⁺	284 [PA-45] ⁺ *213 [PA-45-71] ⁺ 171 [PA-45-42-71] ⁺
4	257 [M+45] ⁺	215 [PA-70] ⁺ *187 [PA-70] ⁺ 173 [PA-(2x42)] ⁺
	259 [M+47] ⁺	214 [PA-45] ⁺

^aAsterisk denotes most abundant daughter ion.

COMPARATIVE STUDY OF RDX AND HMX BY DEPMS AND TSLC/MS

T. H. CHEN

*U. S. Army Armament Research, Development, and
Engineering Center Picatinny Arsenal, New Jersey
07806-5000, U. S. A.*

ABSTRACT. The direct exposure probe mass spectrometry (DEPMS) procedure developed is briefly described and the capabilities of DEPMS in providing the molecular weight and the structural information for RDX and HMX, especially at trace levels, are compared with those of thermospray liquid chromatography/mass spectrometry (TSLC/MS).

1. Introduction

In the identification of unknown compounds, the molecular weight and the structural information are crucial. In the last several years, we have been developing DEPMS procedures to obtain such information for rapid identification of unknown explosives and propellants, especially RDX and HMX. The objective of this paper is to compare DEPMS and TSLC/MS in providing the crucial information needed in the identification of trace quantities of RDX and HMX.

2. Experimental

2.1. APPARATUS

A Finnigan OWA 1020B gas chromatograph/mass spectrometer

(GC/MS) was employed in the DEPMS experiments. A Vestec Model 201 TSLC/MS was used in the TSLC/MS studies.

2.2. REAGENTS

Solvents used in high performance liquid chromatography (HPLC) was HPLC Grade. Other reagents were used without further purification.

2.3. DEPMS

In the DEPMS experiments, the instrument was operated in the positive ion chemical ionization (PICl) mode using methane as the reagent gas. For sample introduction, several droplets of the sample solution in acetone with a concentration of approximately 1 mg/ml were carefully deposited on the loop of the heating wire. The solvent was allowed to evaporate at room temperature.

The dried sample was introduced into the ion source of the mass spectrometer through the direct solid insertion probe inlet and the scanning program initiated just prior to the insertion of the sample into the ion source in order to prevent loss of more volatile species. The methane gas pressure in the ion source was maintained at slightly above 3.0 Torr. Immediately following the insertion of the sample into the ion source, the sample was heated rapidly at the rate of 10 mA/sec, corresponding approximately to 10 °C/sec, to 1 A. The analysis time was approximately 100 seconds. The direct exposure probe was then backed off from the ion source and flash heated for several seconds at about 1.35 A.

2.4. TSLC/MS

In the TSLC/MS experiments, the instrument was operated in the negative ion (NI) mode with discharge and particle-beam (PB) mode employing 75 % 0.1 M ammonium acetate/25 % acetonitrile and 30 % 0.1 M ammonium acetate/70 % acetonitrile as mobile phases, respectively. 5 µl samples with a concentration of

approximately 1 mg/ml acetonitrile were introduced into the instrument through direct loop injection.

3. Results and Discussion

3.1. DEPMS

1, 3, 5-trinitro-1, 3, 5-triazacyclohexane (RDX) and 1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetraazacyclooctane (HMX) are non-volatile and labile compounds which do not easily provide both the molecular weight and the structural information by any single mass spectrometric technique. We have therefore chosen these compounds to assess the capabilities of various mass spectrometric techniques in providing such information.

Figure 1 shows the mass spectrum of RDX obtained by DEPMS. The latter provides both many diagnostic ions for obtaining molecular weight as well as the fragmentation ions in good abundance. The diagnostic ions include $(M + H)^+$, $m/z = 223$, $(M + H_3O)^+$, $m/z = 241$, $(M + NO)^+$, $m/z = 252$, $(M + C_3H_5)^+$, $m/z = 263$, $(M + NO_2)^+$, $m/z = 268$, and $[M + (M + H)]^+$, $m/z = 445$. The fragmentation ions include $m/z = 149$ and 75 by successive loss of CH_2NO_2 from $(M + H)^+$. Very interestingly, $[M + (M + H)]^+$ also follows the same fragmentation pattern, i. e., losing CH_2NO_2 to form ions with m/z of 371 , 297 , 223 , 149 , and 75 . These assignments are confirmed by the spectra of RDX with six N^{15} (RDX, N^{15} -6, Figure 2) and RDX with six D atoms (RDX, D-6, Figure 3). Thus, for RDX, N^{15} -6 and RDX, D-6, the corresponding diagnostic ions are, respectively, $(M + H)^+$, $m/z = 229$, $(M + H_3O)^+$, $m/z = 247$, $(M + NO)^+$, $m/z = 259$, $(M + C_3H_5)^+$, $m/z = 269$, $(M + NO_2)^+$, $m/z = 275$, $[M + (M + H)]^+$, $m/z = 457$ and $(M + H)^+$, $m/z =$

229, $(M + H_3O)^+$, $m/z = 247$, $(M + NO)^+$, $m/z = 258$, $(M + C_3H_5)^+$, $m/z = 269$, $(M + NO_2)^+$, $m/z = 274$, $[M + (M + H)]^+$, $m/z = 457$. The corresponding fragmentation ions for fragments with m/z of 371, 297, 223, 149, and 75 are 381, 305, 229, 153, and 77 for both RDX, N^15 -6 and RDX, D-6.

Figure 4 shows the mass spectrum of HMX obtained by DEPMS. Both the diagnostic ion, $(M + H)^+$, $m/z = 297$, and the fragmentation ions resulting from successive loss of CH_2NO_2 from $(M + H)^+$, i. e., ions with m/z of 223, 149, and 75 are readily observable.

3.2. TSLC/MS

3.2.1. *NITSLC/MS*. Figure 5 shows the spectrum of RDX. In contrast with DEPMS, the ion intensities are quite low and the spectrum is dominated by an ion with $m/z = 102$, probably $(CH_2NO_2CH_2N)^-$. Further, the abundances of the diagnostic ions attributed to $(M + NO)^-$, $m = 252$, $(M + NO_2)^-$, $M = 268$, and $(M + 102)^-$, $M = 324$, are only 2 % or less. The spectrum of HMX (Figure 6) exhibits similar features to that of RDX. Thus, the ion with $m/z = 102$ dominates the spectrum and the diagnostic ions are $(M + NO)^-$, $m/z = 326$, $(M + NO_2)^-$, $m/z = 342$, and $(M + 102)^-$, $m/z = 398$, with abundance of less than 10 %, somewhat higher than those for RDX.

3.2.2. *PBLC/MS*. Figure 7 shows the spectrum of RDX. The latter exhibits primarily low mass fragments. Only traces (< 0.1 %) of diagnostic ions, M^+ , $m/z = 222$, $(M + NO)^+$, and $(M + NO_2)^+$, $m/z = 268$ are formed under this mode.

In the case of HMX (Figure 8), the spectrum shows mainly low mass fragmentation ions. The diagnostic ions are not observed at all.

4. Conclusion

DEPMS in the PICI mode employing methane as a reagent gas provides both molecular weight and structural information in the same experiment for RDX and HMX. Although preliminary in nature, NITSLC/MS with discharge provides only limited such information. Basically, the latter could not be obtained under the conditions of PBLC/MS.

5. Acknowledgement

This author is greatly indebted to Dr. Christina Hsieh Vestal of Vestal Corporation for providing the TS- and PBLC/MS data.

MASS SPECTRUM
08/16/92 20:17:00 + 0:36
SAMPLE:
COMDS.:

DATA: E031EP #34
CALI: CALTAB #2

DATE: 11-23-1993
FIG: 125596.

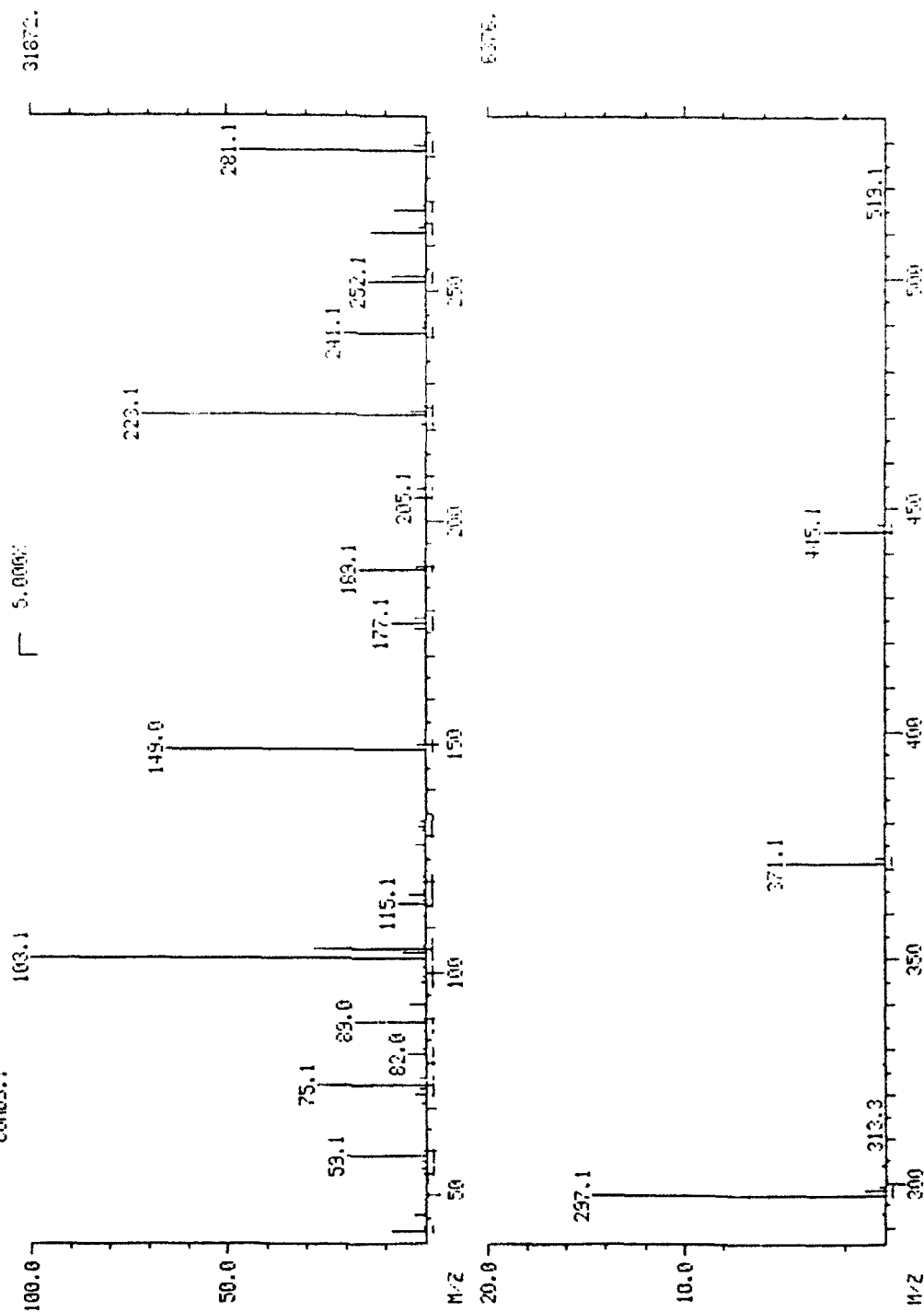


Figure 1. DEPM Spectrum of RDX

MASS SPECTRUM
08/17/92 15:22:00 + 0:45
SAMPLE:
COND.::

DATA: RDX1156 #43
CALI: CALTAB #2
BASE M/Z: 153
RIC: 37792.

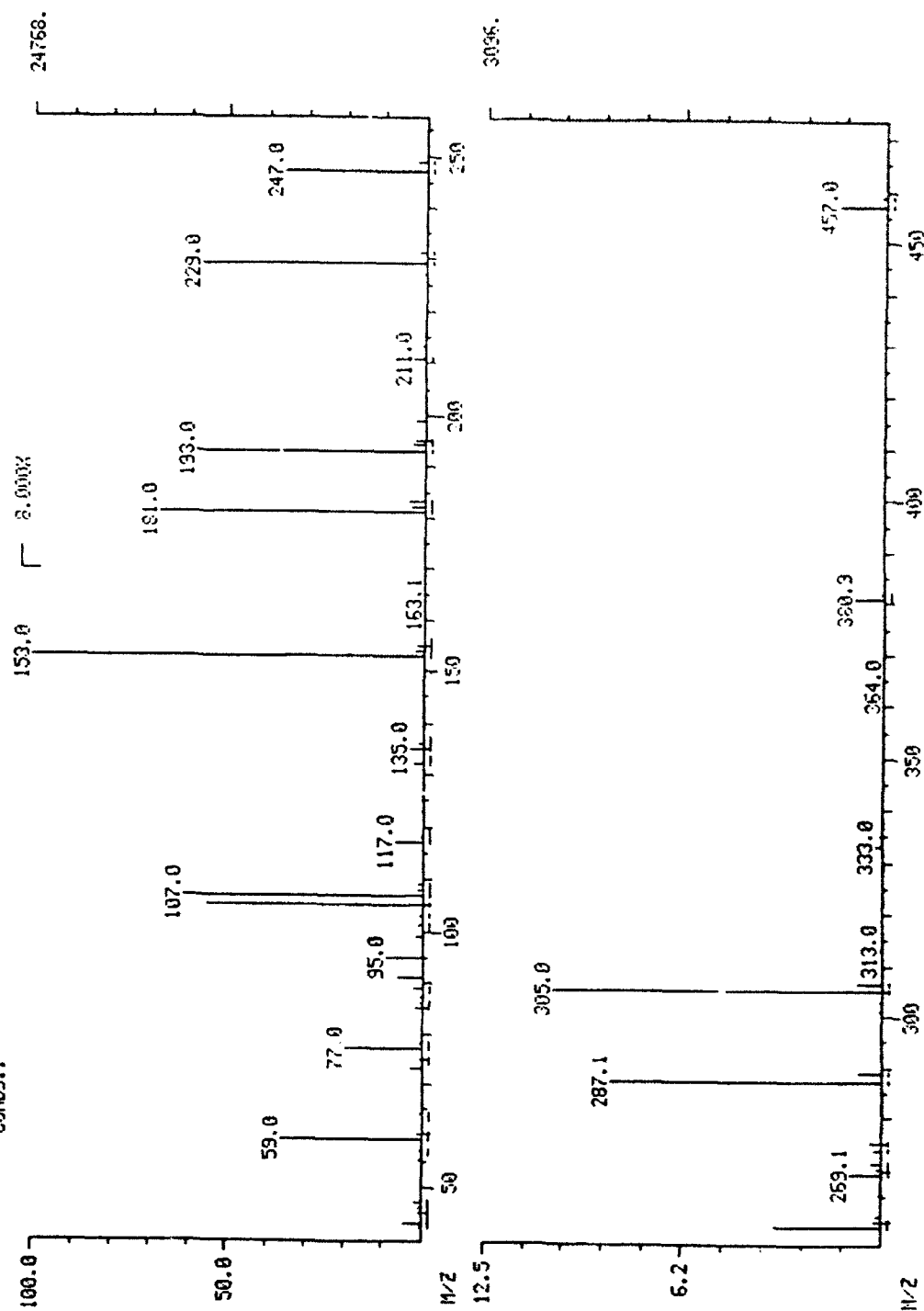


Figure 2. DEPMs Spectrum of RDX, N15-6

MASS SPECTRUM
08/17/92 13:43:00 + 0:23
SAMPLE:
COND.::

DATA: FID: 05 #23
CAL: CALTRAE #2

BASE P/Z: 153
RIC: 63424.

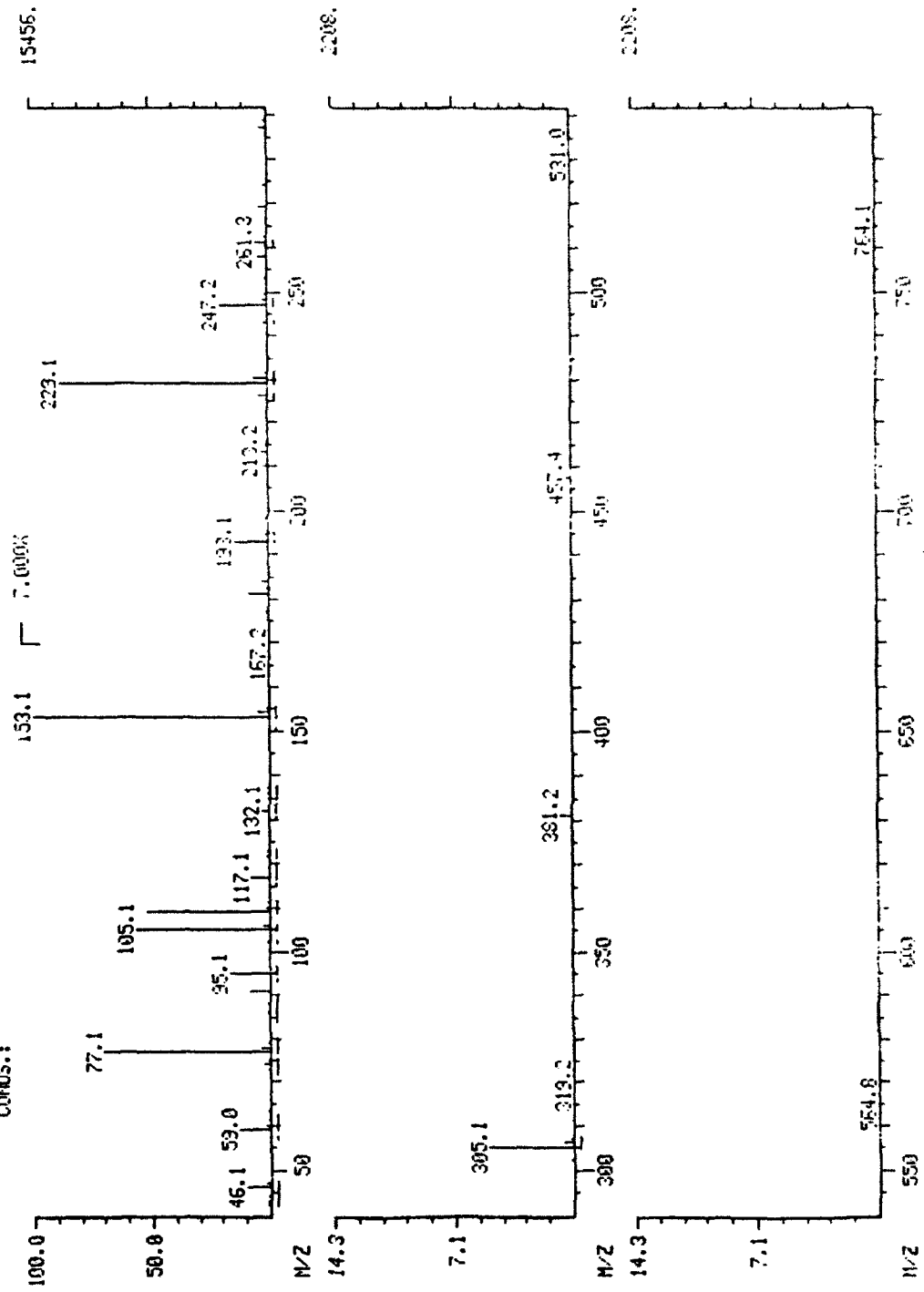


Figure 3. DEPMs Spectrum of RDX, D-6

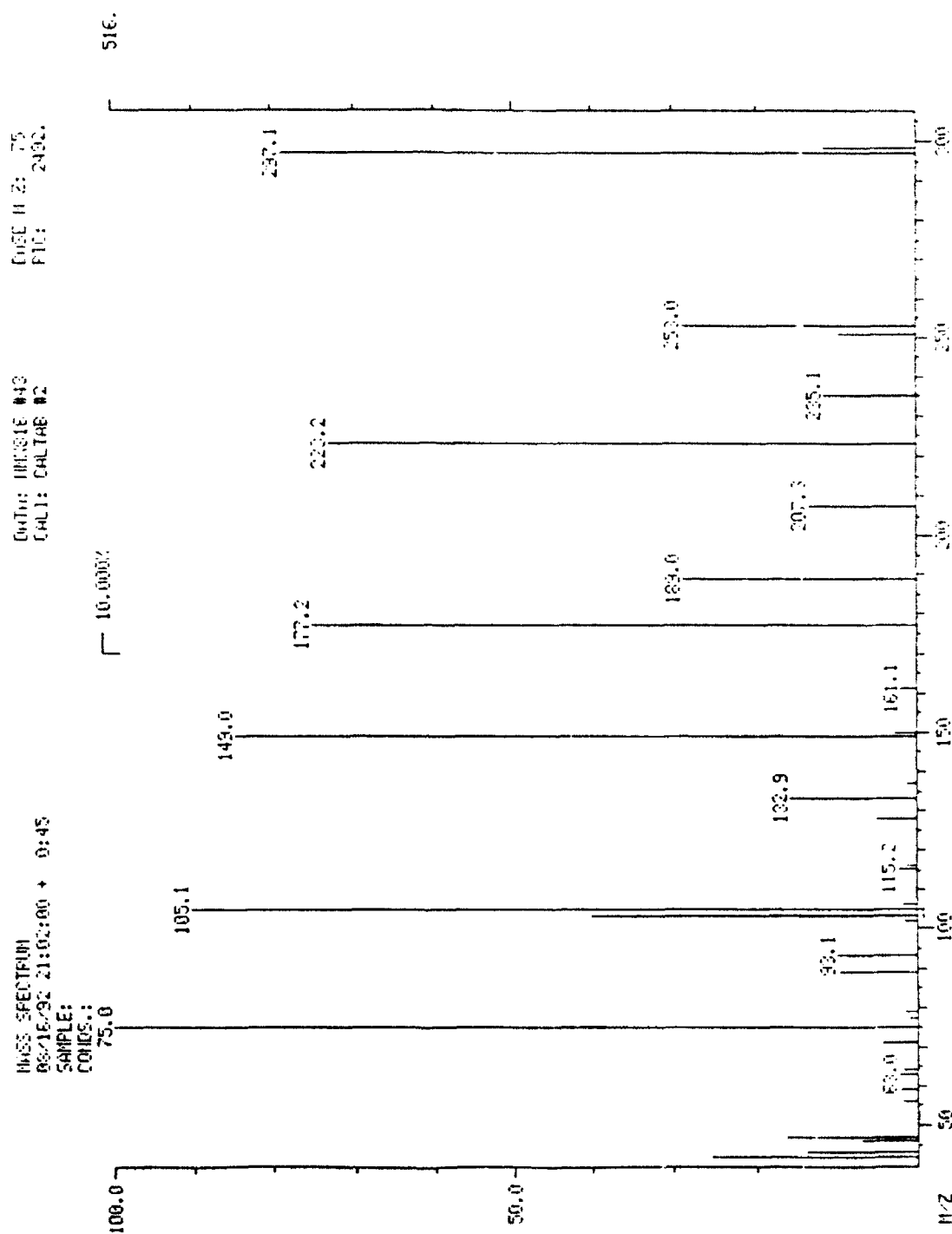


Figure 4. DEPM Spectrum of HMX

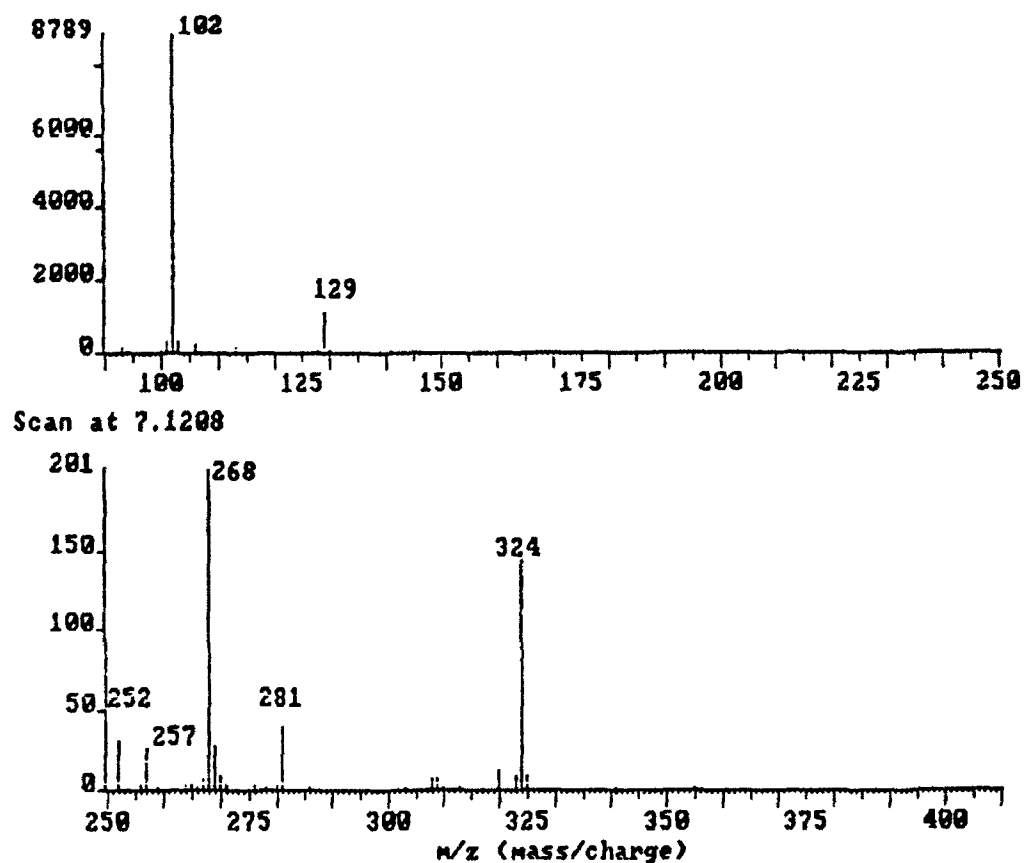


Figure 5. NITSLC/MS (Discharge) Spectrum of RDX

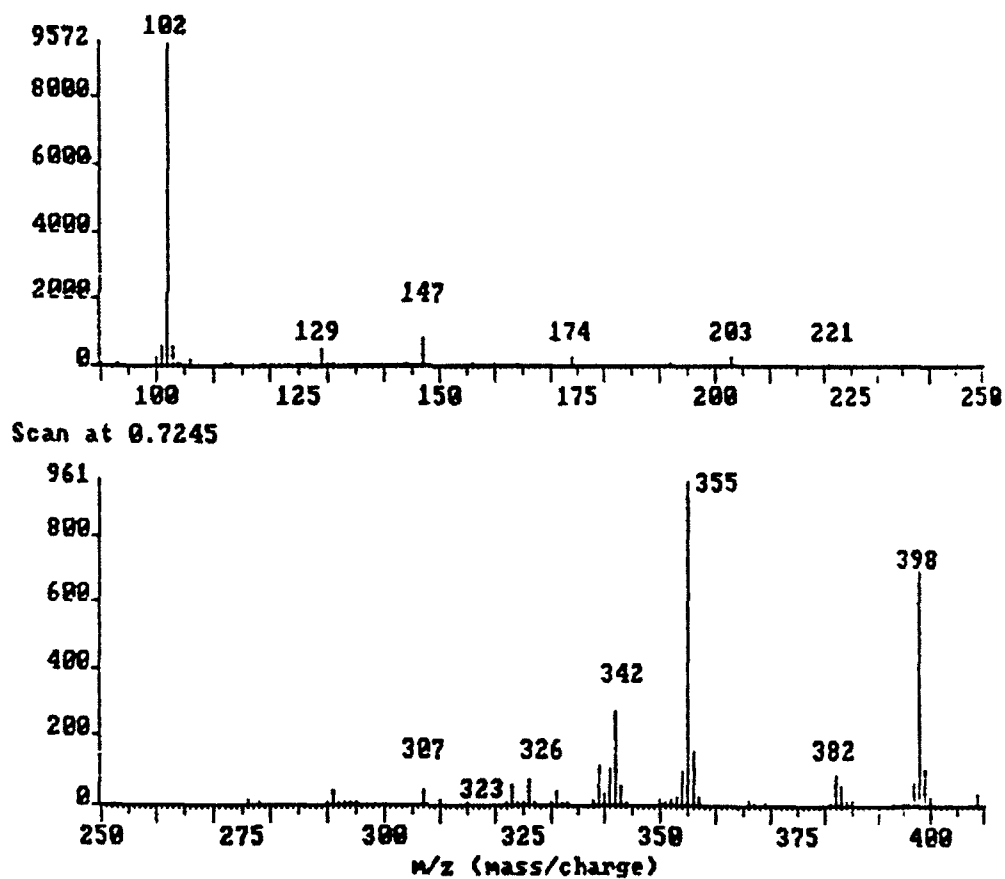


Figure 6. NITSLC/MS (Discharge) Spectrum of HMX

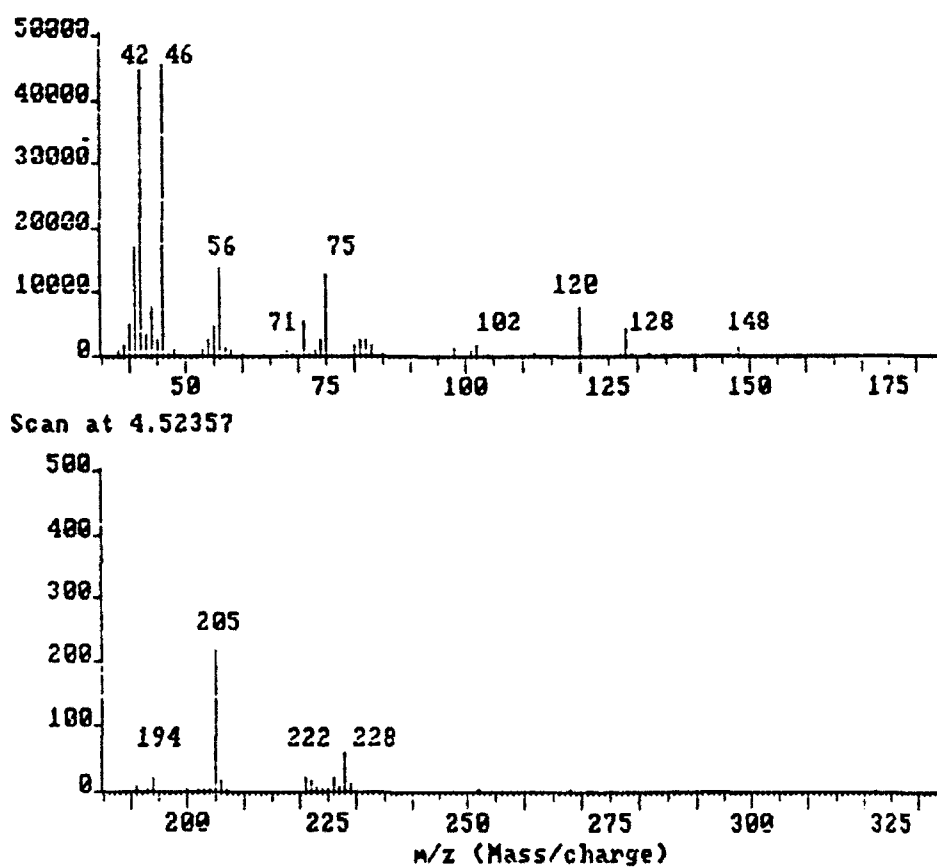


Figure 7. PBLC/MS Spectrum of RDX

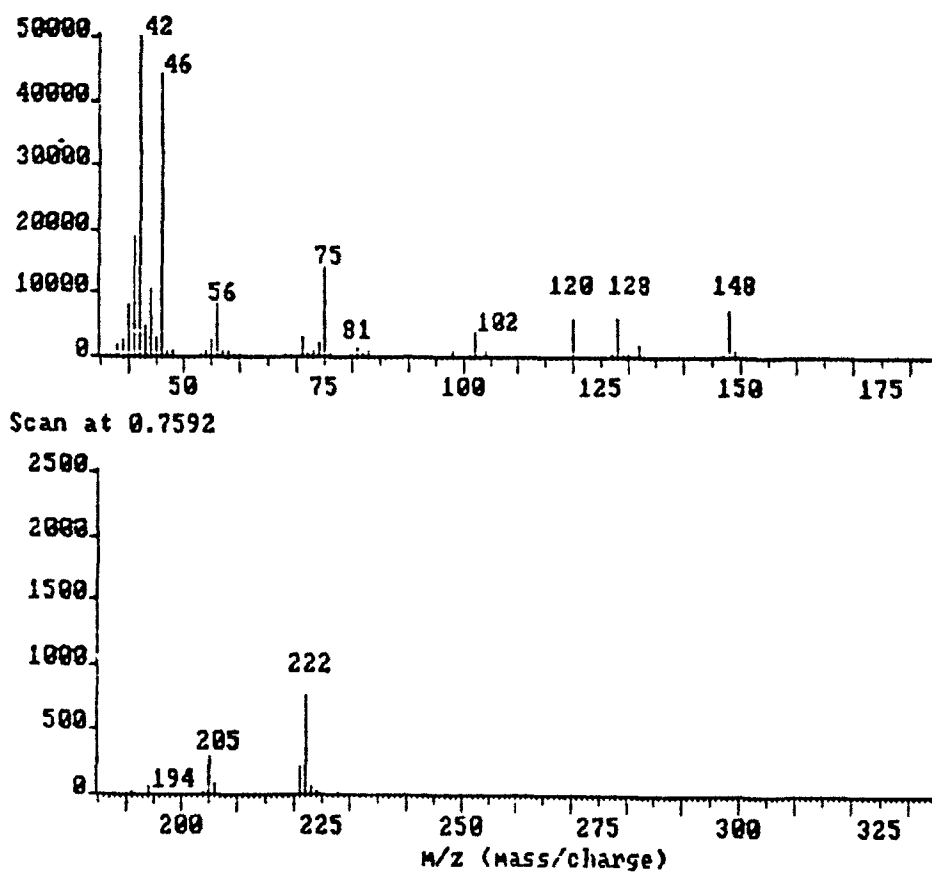


Figure 8. PBLC/MS Spectrum of HMX

GC/MS ANALYSIS OF PETN AND NG IN POST-EXPLOSION RESIDUES

T. TAMIRI, S. ZITRIN, S. ABRAMOVICH-BAR, Y. BAMBERGER. Division of Identification and Forensic Science, National Police Headquarters, Jerusalem 91906, Israel.
J. STERLING, Teva Pharmaceutical Industries, Jerusalem, Israel.

Abstract

GC/MS is used in our laboratory to confirm the identity of explosives in post-explosion debris.

The GC/MS analysis of PETN has often been unsuccessful, mainly due to its thermal decomposition under GC conditions. Changing experimental conditions, using a very short (1.5 m) capillary column, solved the problem.

PETN in post-explosion samples was reported to be occasionally accompanied by its degradation products. We have found a similar behaviour of NG in actual post-explosion samples. The TLC plates of these samples contained several Griess - positive spots which corresponded to mono- and dinitrate esters of glycerol. These esters were independently synthesized and characterized. Their analysis was carried out using silylation, GC/EIMS and GC/CIMS. It is suggested that the identification of nitrate esters of pentaerythritol (other than PETN) and glycerol (other than NG) can be used to prove the original presence of PETN and NG in the debris.

Introduction

Post-explosion residue analysis remains a problematic field in forensic laboratories. As GC/MS is the method of choice for organic analysis in our laboratory, we try to use it routinely in post-explosion residue analysis. This is according to our policy not to base an identification of a single organic compound on chromatographic methods only [1,2].

While this policy is easily applied to nitroaromatic explosives (such as TNT), its application to nitrate esters or nitramines has often been unsuccessful. Thermal instability of some of these compounds (e.g. PETN) or low volatility of others (e.g. HMX) cause difficulties in their GC/MS analysis.

The two common nitrate esters encountered in our laboratory are pentaerythritol tetranitrate (PETN) and glycerol trinitrate ("nitroglycerin", NG).

Another difficulty in the GC/MS analysis of nitrate esters is the similarity between their EI mass spectra. Thus, the EI spectra of PETN and NG, shown in Figure 1, are practically indistinguishable from each other, containing abundant ions at m/z 30 (NO^+), 46 (NO_2^+) and 76 ($\text{CH}_2\text{ONO}_2^+$) but no molecular ions.

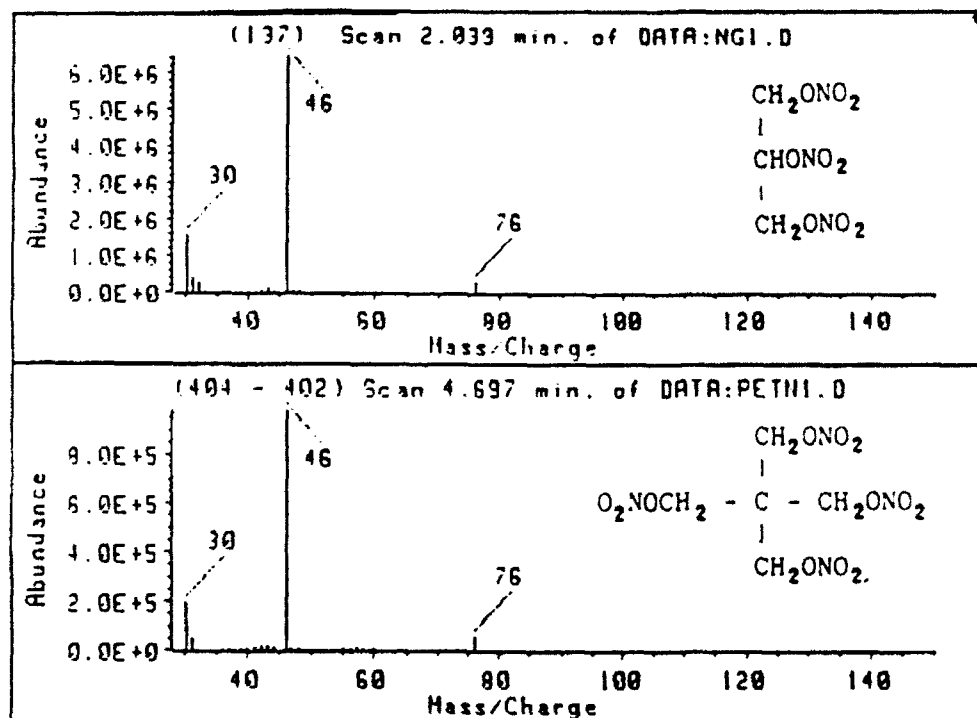


Figure 1. EI mass spectra of NG and PETN.

Obviously, PETN and NG have different GC retention times but this means that their identification is based on chromatographic properties. To individualize nitrate esters by mass spectrometry, the chemical ionization (CI) mode is used. The CI mass spectra of NG and PETN, shown in Figure 2, contain highly abundant $[\text{M}+\text{H}]^+$ ions as well as major fragment ions corresponding to $[\text{M}+\text{H}-\text{HONO}_2]^+$.

However, the use of GC/CIMS in our instrument (see Experimental) was accompanied by a decrease in sensitivity. As a result, there were often post-explosion samples which gave Griess-positive spots corresponding to PETN or NG in TLC, but could not be analysed by GC/MS. This paper describe some ways to overcome the problem.

Results and Discussion

To minimize thermal decomposition of the nitrate esters, our standard (15 m) capillary column was replaced by a very short (1.5 m) column. The improvement in the sensitivity is clearly demonstrated in Table 1. The numbers in Table 1 are ratios between minimal amounts of the

explosives, from which a full mass spectrum could be obtained in the long column and in the short column. The increased sensitivity obtained with the short column is clearly seen in the GC/EIMS of RDX, PETN and NG. Even more important was the ability to obtain a discrete chromatographic peak in the short-column GC/CIMS analysis of PETN, while no such peak was obtained with the long column.

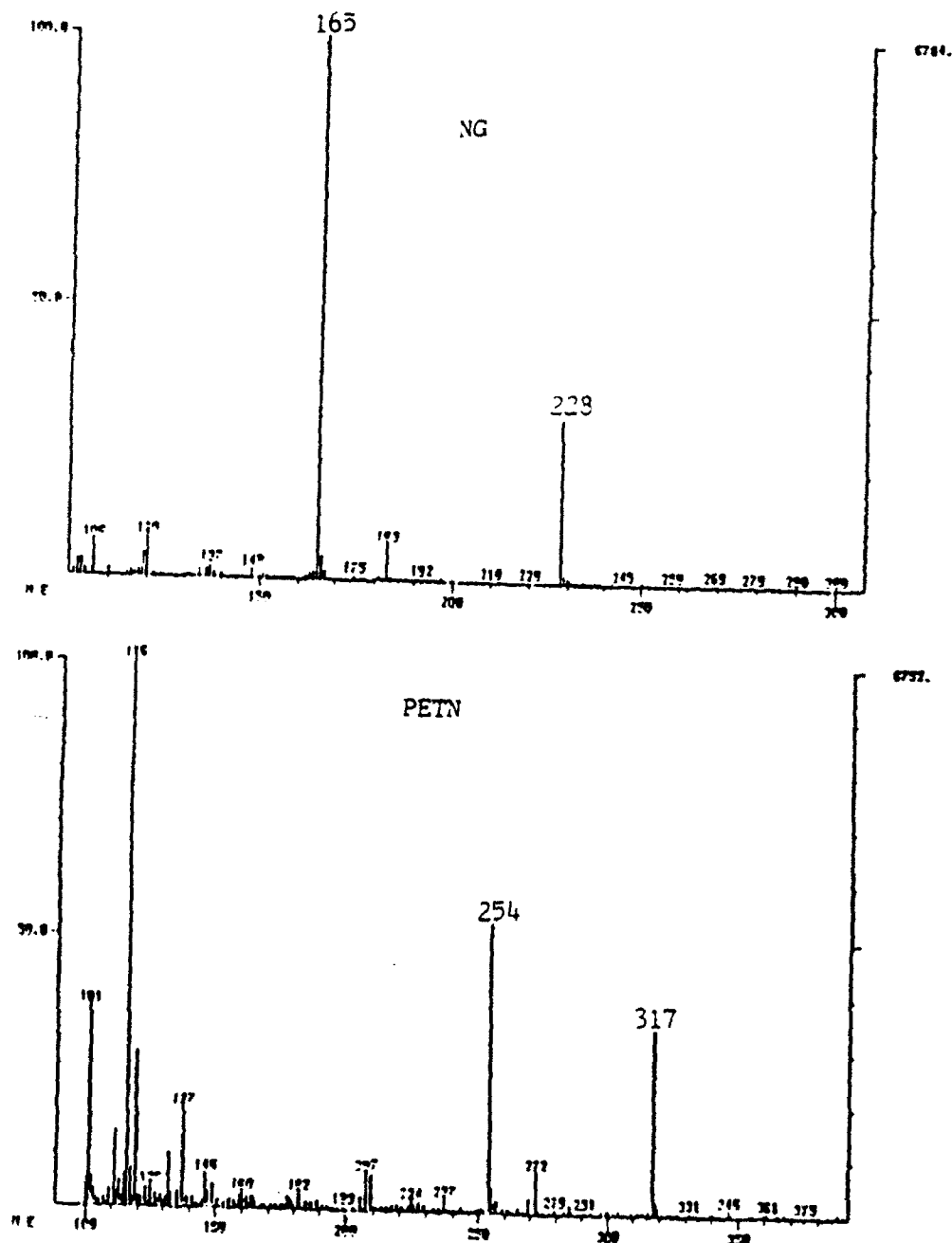


Figure 2. CI mass spectra of NG and PETN.

TABLE 1. Comparison of long vs. short column for minimum detection limit of some explosives.

	SENSITIVITY (SHORT COLUMN - 1.5 M)	
	SENSITIVITY (LONG COLUMN - 15 M)	
	GCEI	GCCI
PETN	50	*
NG	1000	8
RDX	20	4
TETRYL**	4	4
DNT	5	20
TNT	5	20
HEROIN	1	1

* No data obtained in long column.

** Data of decomposition product.

The lower part of Figure 3 shows the total ion chromatogram (TIC) and the mass chromatograms of a post-explosion extract from an actual case. The mass chromatograms, recorded at m/z 254 and 317, allowed to single out the chromatographic peak of PETN. Locating this peak in the TIC was practically impossible. This chromatographic peak gave a CI mass spectrum which corresponded to PETN, shown in the upper part of Figure 3.

Another way to tackle the problems encountered in the GC/MS analysis of nitrate esters was based on an earlier finding [3]: post-explosion residues from cases involving PETN sometimes included lower nitrate esters of pentaerythritol (PE). Recently, we have found a similar phenomenon in NG-related cases, where lower nitrate esters of glycerol were identified. They had previously been tentatively identified by TLC analysis of post-explosion residues [4]. These lower nitrate esters of the parent alcohol (PE or glycerol) were formed by partial hydrolysis of PETN or NG during or after the explosion.

It occurred to us to use the presence of these lower esters, which at first seemed to complicate the post-explosion analysis, as evidence for the original presence of PETN or NG. As these esters contain free hydroxyl groups, they can be easily silylated and the resulting TMS derivatives are suitable for GC/MS analysis.

This method, albeit indirect, can positively confirm the original presence of PETN and NG.

In order to use this method, we have synthesized the lower nitrate esters of PE and glycerol. The mono-, di- and trinitrate esters of PETN were prepared by hydrolyzing PETN and separating the resulting esters by column chromatography [3,5].

The two isomeric dinitrate esters of glycerol (1,2-GDN and 1,3-GDN) were prepared by partial nitration of glycerol followed by chromatographic

separation [6]. The two isomeric mononitrate esters (1-GMN and 2-GMN) were prepared according to the procedure shown in Scheme 1 [7-10].

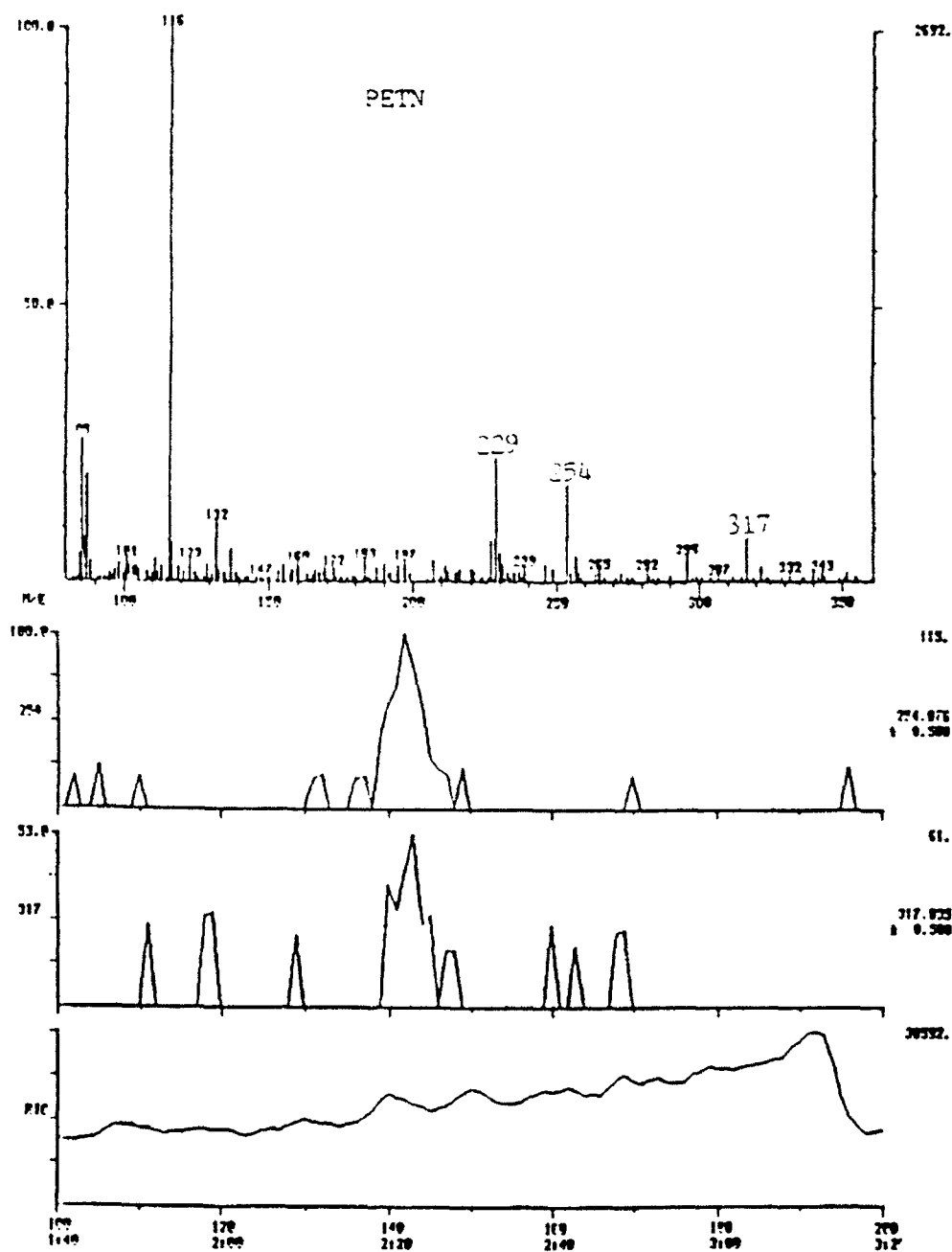
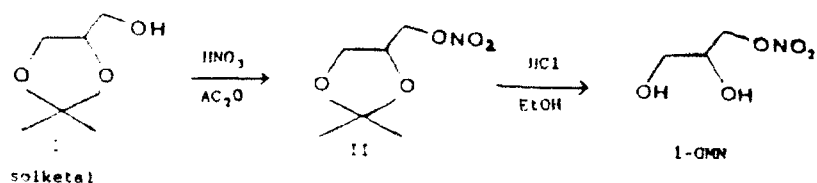


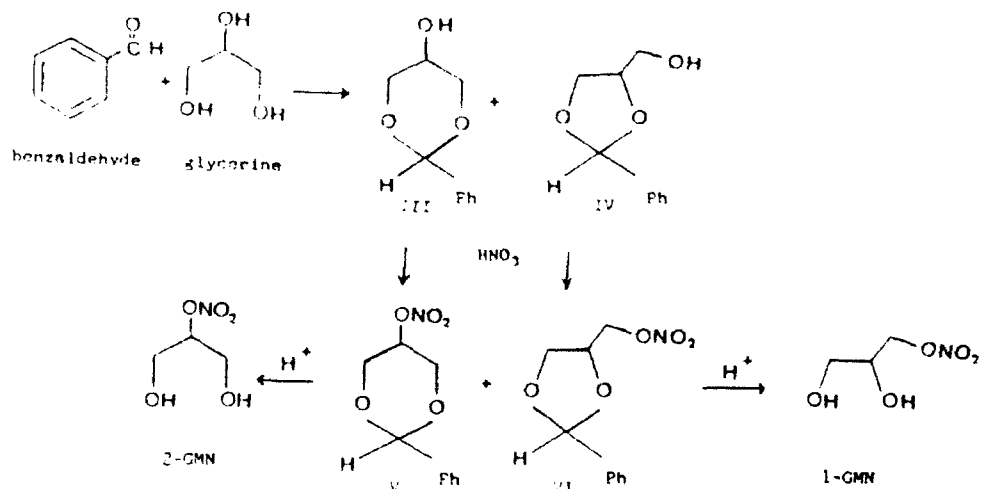
Figure 3. TIC, mass chromatograms and mass spectrum of an extraction of a real case containing PETN .

Scheme 1. Synthesis of 1-GMN and 2-GMN

Synthesis of glycerine-1-mononitrate



Synthesis of glycerine-2-mononitrate



All these esters were silylated and the resulting TMS derivatives were characterized by GC/MS, in both EI and CI modes. In all PE nitrate esters as well as in the GDN isomers, we have obtained only one silylation product, which corresponded to the fully silylated derivative. The GMN isomers also gave the fully silylated, di-TMS derivatives, but another chromatographic peak was present. It could correspond to the mono-TMS derivative but its final identification has not yet been carried out.

The next step was the application of this method to post-explosion samples from actual cases. In one case, where the TLC analysis showed several Griess-positive spots in addition to PETN, the extract was silylated and subjected to GC/MS.

The PE-trinitrate-TMS derivative was clearly identified, as shown in Figure 6. This could be viewed as strong evidence to the original presence of PETN.

In another case, the identification of the TMS derivative of GMN, shown in Figure 7, served as evidence to original presence of NG.

Figure 4 shows CI mass spectrum of the PE-trinitrate-TMS derivative and Figure 5 shows EI mass spectrum of GMN-TMS derivative.

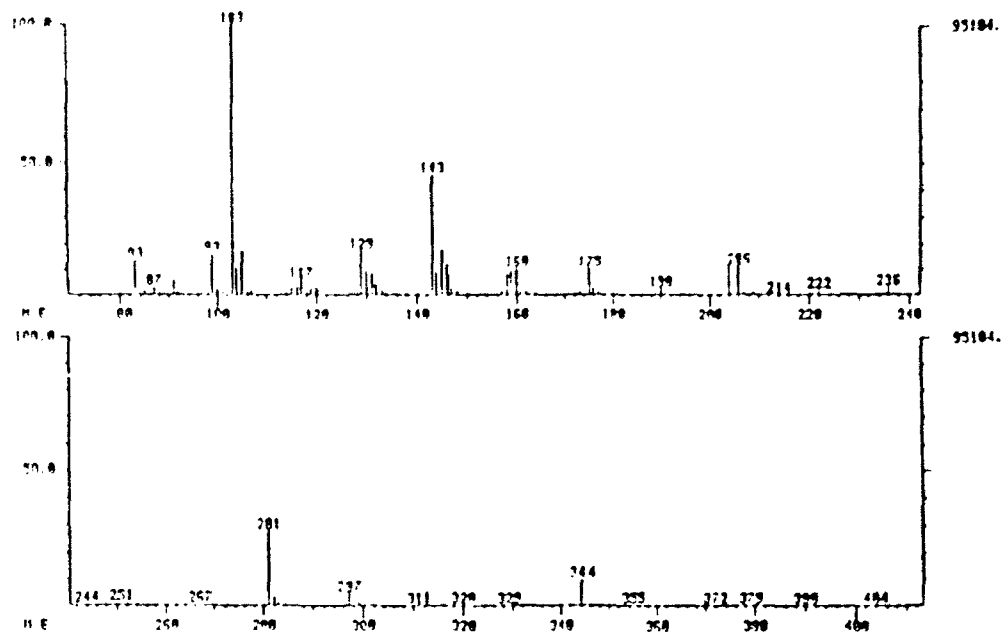


Figure 4. CI mass spectrum of PE-trinitrate-TMS derivative.

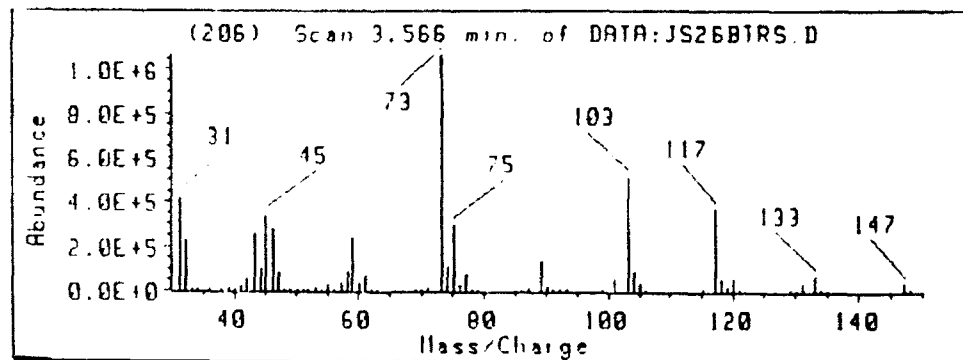


Figure 5. EI mass spectrum of GMN-TMS derivative.

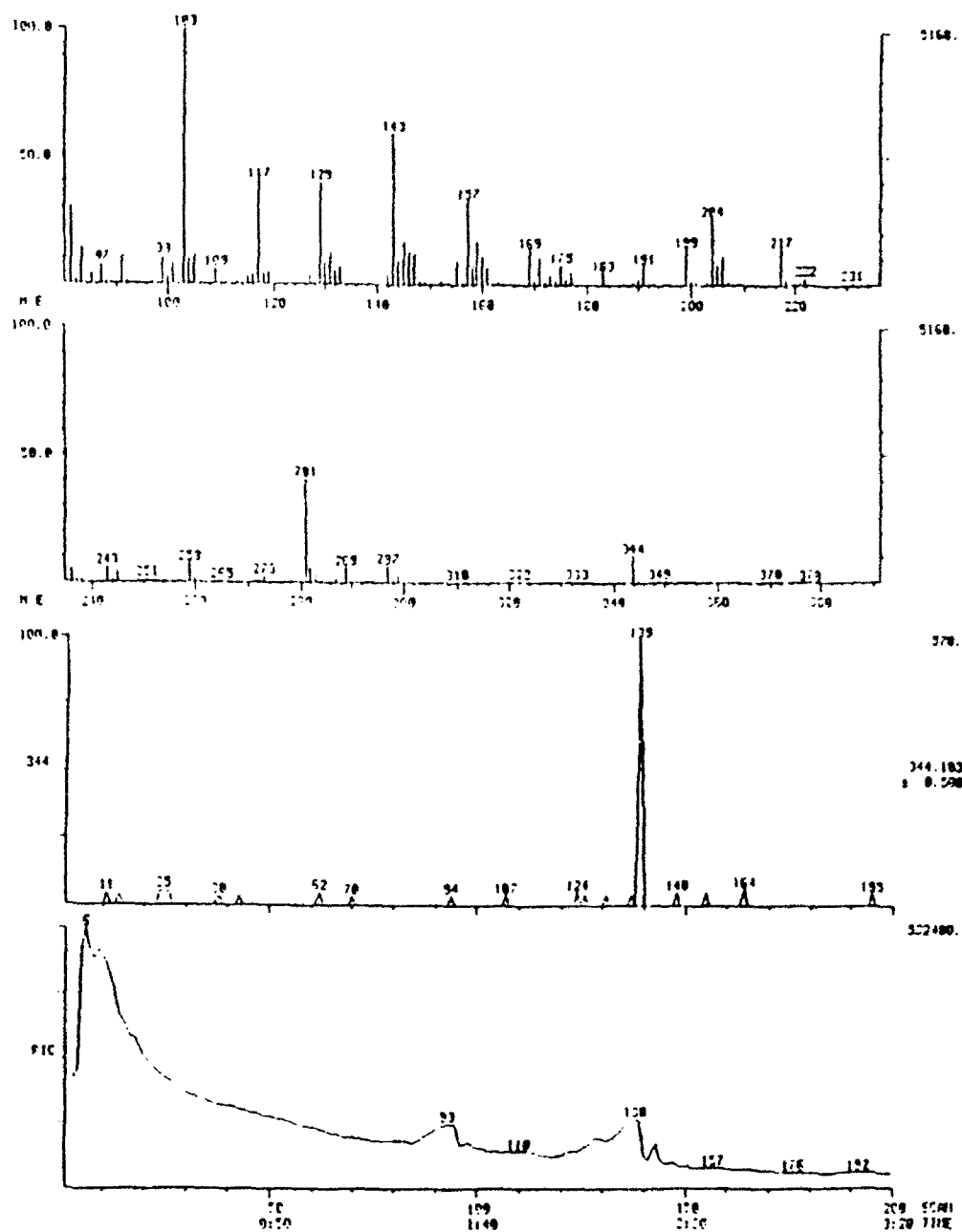


Figure 6. TIC, mass chromatogram and CI mass spectrum of a silylated extract from a real case containing PETN.

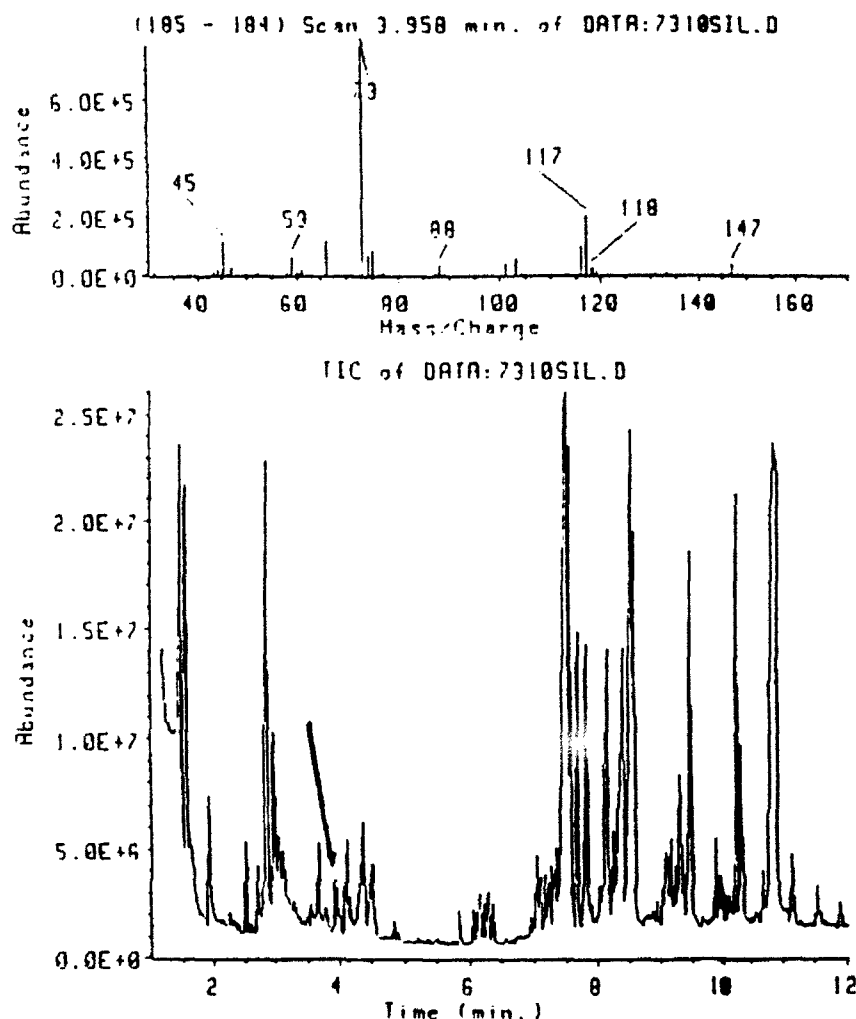


Figure 7. TIC and EI mass spectrum of a silylated extract from a real case containing NG.

Experimental

GC/MS was done on a Finnigan 4500 quadrupole mass spectrometer and on HP-MSD quadrupole mass spectrometer. The GC columns were :1) RSL-200, 15 m X 0.25 mm (I.D.) with 0.25 μ m coating of DB-5. 2) RSL-200, 1.5 m X 0.25 mm (I.D) with 0.25 μ m coating of DB-5. Temperatures were programmed from 60°C to 220°C at 20 deg/min. Injector temperature was 180°C. Transfer line temperature was 220°C. Ion source temperature was 140°C. Scan range was 40-500 mass units. Scan rate was 1 scan per second. Electron energy 70 eV. Helium was the carrier gas. Methane was the CI reagent gas.

Preparation of nitrate esters of PE.

To a refluxing solution of 15.8 gr of PETN in 60 ml of ethanol : dioxane (1:1) was added during 1 hour, 7 gr of hydrazine hydrate (80% aqueous solution). During the next 3 hours additional 5 gr of hydrazine was added. At the conclusion of the reaction there was almost no PETN, much tri- and dinitrate as well as some mononitrate. Ethanol (30 ml) was added and the solution concentrated in vacuo to 14.5 gr of a viscous yellow oil. This was triturated three times with 20 ml portions of water. The combined water fractions were then extracted two times with 60 ml portions of ether.

The ether extract and water-insoluble fraction were combined and concentrated to a viscous oil (ca. 11.5 gr). A portion of this material (7.2 gr) was flash column chromatographed eluting with ethyl acetate/methylene chloride (1:9) to isolate 3.1 gr of a pale yellow oil identified as the trinitrate. Elution with ethyl acetate/methylene chloride (1:1) gave the dinitrate as a pale yellow oil, 3.2 gr. The water solution (from above) was treated with 2N H_2SO_4 (ca 7 ml), neutralized with ammonium hydroxide and concentrated in vacuo to a biphasic oily mixture (2.9 gr). This was triturated three times with 20 ml portions of methanol leaving a white oil which crystallized overnight and was identified as pentaerythritol (2 gr).

The methanol was removed in vacuo leaving 0.9 gr of yellow oil. The addition of a few ml of acetone induced a small amount (ca. 0.1 gr) of precipitate also identified as pentaerythritol. The mother liquor was purified by flash column chromatography eluting with ethyl acetate to isolate 0.6 gr of a golden oil. Crystallization was induced by the addition of chloroform to give 0.5 gr of the desired mononitrate as a slightly yellow solid, m.p. 71-76°C.

Preparation of 1,2- and 1,3 - GDN :

To a solution of 48.9 g of sulfuric acid, 16.5 gr of nitric acid and 6.6 gr of water was added dropwise with stirring 15 gr of glycerol maintaining temperature at ca. 20°C during 15 min. After an additional 10 min the solution was poured into 450 ml of cold water and extracted as follows: twice with hexane to remove most of the GTN; three times with ether to remove the GDN's and twice with methylene chloride to remove the GMN's. The ether fractions were dried, concentrated and further purified by flash column chromatography eluting with ethyl acetate/hexane (15:85) to isolate 1,3-GDN (3.3 gr) and 1,2 GDN (0.6 gr).

Preparation of 1-GMN:

A. Preparation of 2,2-Dimethyl-4-nitroxymethyl-1,3-dioxolane (II):

To a solution of 10 gr of solketal in 12 ml of acetic anhydride at 0°C was added dropwise a cold solution prepared from 5 gr of fuming nitric acid in 12 ml of acetic anhydride. The solution was stirred an additional 10 min and poured into ice water containing sodium bicarbonate. This mixture was stirred until bubbling ceased and the cloudy aqueous phase extracted once with diethyl ether. The ether solution was washed with saturated bicarbonate until neutral to give

12 gr of crude product relatively pure by TLC. The desired compound was isolated by flash column chromatography eluting with ethyl acetate/hexane (1:9) to give 8 gr of the pure title compound (II) as a clear colorless oil.

B. Preparation of 1-GMN:

A solution of 7 gr of II and 1 ml of conc. HCl in 70 ml of abs. ethanol was heated at reflux for 3.5 hours at which time it was concentrated in vacuo to 6 gr of a clear colorless oil relatively pure by TLC. This was purified by flash column chromatography eluting with ethyl acetate/hexane (5:2). Fractions containing pure 1-GMN were combined and evaporated to 3 gr.

Preparation of 2-GMN.

A. Preparation of 4-Hydroxy-2-phenyl-1,3-dioxane(III) (and 4-hydroxymethyl-2-phenyl-1,3-dioxolane (IV)) :

A mixture of 64.5 gr of freshly distilled benzaldehyde and 47 gr of glycerol was heated at 145-150°C for 1.5 hours (without condenser) and a further 2 hours at 165°C. After cooling, the reaction was washed three times with water, dissolved in ether and again washed three times with water. The ether layer was dried and concentrated in vacuo and the residue extracted three times with hexane. The hexane-insoluble fraction (ca. 47 gr) was distilled at 2 mmHg. The fraction distilling at 125 - 135°C was collected to give ca. 20 gr of III + IV.

B. Preparation of 4-Nitroxy-2-phenyl-1,3-dioxane (V) (and 4-nitroxy-2-phenyl-1,3-dioxolane (VI)) :

To a solution of 6.6 g of mixed phenyl dioxolane/dioxane alcohols (III+IV) in 16 ml of acetic anhydride at 0°C was added dropwise a cold solution prepared from 6.6 gr of fuming nitric acid in 16 ml acetic anhydride. Work-up as above gave a complex product mixture which was purified by flash column chromatography eluting with ethyl acetate/hexane (1:9). Fractions containing predominantly compound VI contaminated with the two GDN isomers were collected, combined (2.2 gr) and rechromatographed eluting with methylene chloride/hexane (1:9). Fractions containing the cis/trans isomeric mixture of VI were evaporated to give 1.5 gr. NMR and GC/MS confirmed a cis/trans mixture of the unsymmetrical nitro compound.

From the original column, fractions containing predominantly V, contaminated with 1,2-GDN, were combined and evaporated to 1.6 gr of an oily white solid which was crystallized from cold ether to 0.75 gr of V, m.p. 80-85°C.

C. Preparation of 2-GMN :

A solution of 0.55 gr of V and 10 drops of conc. HCL in 5 ml of abs. ethanol was heated at reflux for 3.5 hours at which time it was concentrated in vacuo. This was purified by flash column chromatography eluting with ethyl acetate/hexane (3:2) to give 0.2 gr of 2-GMN as a clear colorless oil. NMR, IR and MS supported the proposed structure.

Silylation of alcohols:

Tri Sil reagent (Hexamethyldisilazane with trimethylchlorosilane in pyridine) was added to a small amount of the alcohol in a sealed ampule. The mixture was heated at about 70°C for 20 minutes.

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NUCLEAR BASED EXPLOSIVE DETECTION SYSTEMS-1992 STATUS

Tsahi Gozani and Patrick M. Shea
Science Applications International Corporation
2950 Patrick Henry Drive
Santa Clara, CA 95054, U.S.A.

ABSTRACT. Over the past several years the attitude towards nuclear based explosive detection systems (EDS) has fluctuated between euphoria to disappointment. This had to do little with technical merits and more with a host of other issues raging from changing perceptions of threats and resulting systems' requirements, to the effect of security regulations on the health of the commercial airline industry. Despite these tribulations, progress continues. Six thermal neutron analysis (TNA) EDS's have been deployed in several airports in the U.S.A. and abroad. While providing the users with valuable security services, a large amount of data has been collected, allowing further improvements. Indeed the currently deployed TNA systems are an improved version of the first one installed in 1989 at the JFK International Airport's TWA terminal. Significant additional enhancements in performance, which resulted from recent laboratory studies are awaiting approval for implementation in the existing systems.

In the last few years the desire to detect ever smaller amounts of explosives led to the exploitation of fast neutron reactions. Progress in the development of the pulsed fast neutron analysis (PFNA) technique, as the ultimate EDS in terms of sensitivity, low false alarm rate and high throughput capability, are reported. Other nuclear based techniques such as the gamma and neutron resonance attenuation (GRA and NRA, respectively) are briefly discussed and compared on their own as well as within the concept of a "system of systems." The latter may incorporate several sensors and other attributes of security to provide the most effective system.

1. INTRODUCTION

Three years ago in Manheim, Germany, when the Pan Am 103 disaster was fresh in our minds, we presented the status of explosive detection technologies based on nuclear techniques. Since that time, the political upheaval caused by that disaster in the U.S. and the momentous changes in world geopolitics, exemplified by the changes in Eastern Europe, have lead to a period of uncertainty in the technological development of explosive detection systems.

The smaller upheaval in the U.S. is reflected in the President's Commission Investigation and Report, and the Congressional action of Public Law 101-45. These

executive and legislative activities have lead to a large spread of technological efforts which have yet to deliver definitive answers, and a general desire to detect smaller and smaller amounts of explosive. The larger upheaval has led to the perception by some that the threat of terrorism is significantly lower now and hence investment in security measures should be similarly reduced. This is supported by the airlines, all of whom are operating in a more difficult financial environment. Both upheavals have significantly slowed the development and implementation of nuclear-based explosive detection systems (EDS) over the last three years.

In fact, a two-tier development program is emerging in the U.S. and elsewhere. On one level, automated, objectively testable systems based primarily on a variety of nuclear reactions are being developed as a long-term research effort. These systems are directed at being demonstrably high performance, i.e.: high detection rates, low false alarm rates, automatic operation and focused on small amounts of explosives. They are also considered to be bulky, expensive, and thus difficult (and hence, some argue, unlikely) to be deployed. Such systems are exemplified by the Thermal Neutron Analysis (TNA) systems and technologies under development like the Gamma Resonance Attenuation (GRA), Pulsed Fast Neutron Analysis (PFNA), and others.

The second tier are those systems which are modifications of conventional devices, such as improved X-ray machines, vapor and particulate detectors, and passenger profiling techniques. These systems are not fully automatic, either in the interpretation stage (X-rays) or in the acquisition stage (profiling and vapor detectors). Such systems are much more difficult to objectively assess, because, among other factors, they depend on the quality of the operator. Some of the systems, e.g., X-rays, are not explosive detectors per se, but may detect some related characteristics of explosives as sometimes used in bombs. It is intuitively (though not always quantitatively) clear that these systems, even in their present form, do provide an improvement over current imperfect airport security systems. Hence, there are significant efforts in both government and industry to study and improve these systems. The (relatively) lower cost, more compact size, and lack of rigorous performance test procedures make them less controversial and more acceptable.

One welcome development over the last few years, is that finally there is an almost unanimous, though belated, acceptance that the ultimate security performance will be achieved if an array of complementary techniques or "system of systems" (appropriately called by some, SOS) is employed. Each individual system is used at its best and the performance of the integrated system is far better than its individual components.

The progress in the nuclear based EDS is described below, concluding with a brief discussion of the system of system approach.

2. NUCLEAR BASED EDS - GENERAL

Nuclear techniques offer capabilities which are essential to effective detection devices. These are: high penetrability, high specificity, high speed, non-intrusiveness and the possibility of automatic decision making. The generic nuclear based interrogation technique is shown in Figure 1. The key components are a source of penetrating radiation, means to tailor the radiation (e.g., slow down neutrons or collimate them) the interrogated object (i.e., suitcase), means of detection (e.g., NaI(Tl) scintillation counter), and means of collecting and processing of the received data to make a decision on the presence of the contraband. The various elemental nuclei in the interrogated object react in different ways

(i.e., they have different interaction cross-sections) with the interrogation radiation. Generally, they emit detectable characteristic radiations, i.e., high energy gamma rays. All explosives and especially all known commercial and military explosives have distinctive elemental compositions. They are generally dense and are rich in oxygen and nitrogen, and relatively poor in carbon and hydrogen when compared to common benign substances.

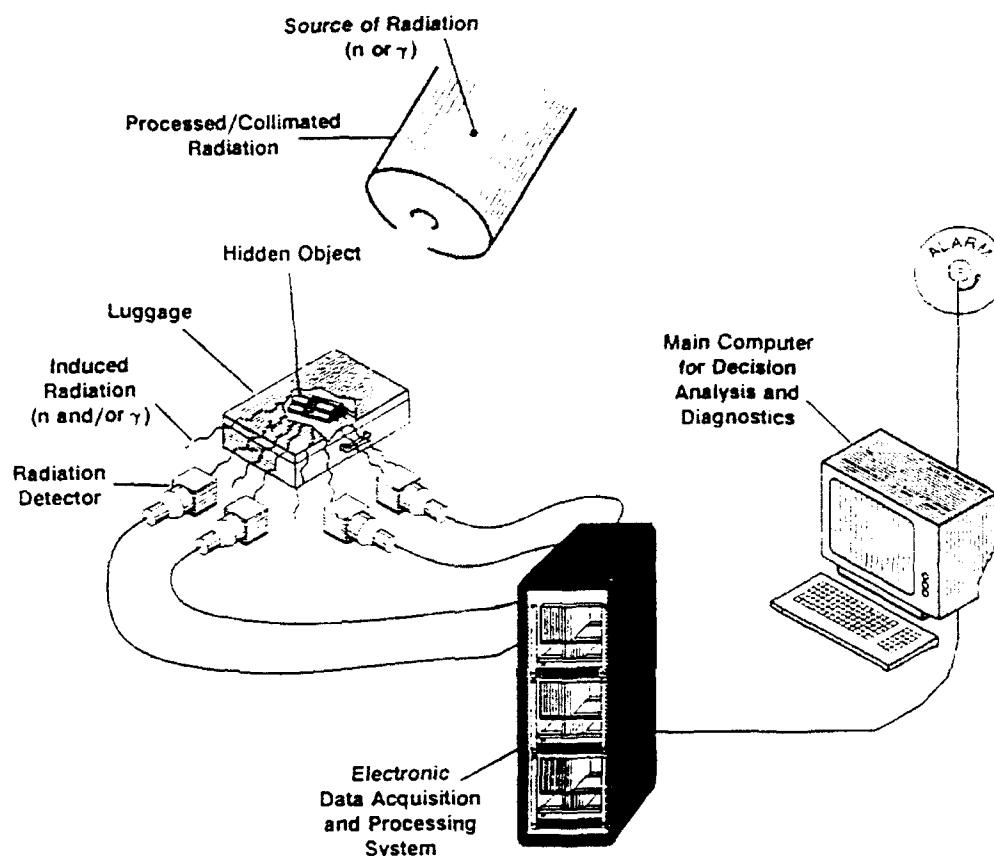


Figure 1. Diagram of a generic active nuclear based explosive detection system.

The intensity, energy and spatial distribution of the detected radiations, their relation to the probing radiation and any additional available (including *a priori data* such as profiling) information concerning the object are used in the decision process.

Nine nuclear based techniques are listed in Table 1, along with the probing radiation, main nuclear reaction, detected radiation and radiation sources. The techniques, except for the last two, are based on neutron interrogation. The first five use as prime signatures the gamma-rays produced by the different nuclear reactions. The sixth and seventh techniques use the resonance scattering of the probing neutrons and gamma rays, respectively, as a means of detection. The last one uses the low energy gamma rays emitted from photonuclear activation of nitrogen.

TABLE 1. Key generic features of nuclear based techniques relevant to explosive detection.

#	Technique	Probing Radiation	Main Nucl. Reaction	Detected Radiation	Sources	Primary/Secondary Signatures	Comments
1	TNA	Thermalized neutrons	(n, γ)	Neutron capture γ -rays	^{252}Cf , also accel. based sources: (D,D), (D,T), (D,Be), (P,Li), (P,Be), etc.	N Cl, H	Limited view detectors improve spatial resolution, requires stronger source
2	PTNA	Time dependent epi and thermal neutrons	(n(t), γ)	Time dependent capture γ -rays and neutrons	μs pulsed (D,D), (D,T), (D,Be), (P,Li), (P,Be), and others	N Cl, H	Low sensitivity
3	FNA	Fast (high energy) neutrons	(n,n' γ)	γ -rays produced from inelastically scattered neutrons	(D,T)	O, C, N H, Cl	Limited view detectors improve spatial resolution, requires stronger source
4	FNA/PTNA	Fast neutrons and time dependent thermal neutrons	(n,n' γ) + (n(t), γ)	Like PTNA and FNA	μs pulsed (D,T) accel. source	O, C, N H, Cl	Low sensitivity
5	PFNA	Nanosecond (ns) pulses of fast ($E_n > 5$ MeV) neutrons	(n,n' γ)	Like FNA	ns pulsed (D,D) accel. with $E_d \sim 6$ MeV	O, C, N, Cl, Others Metals, Si, Others	Imaging methods improve S/N* for the direct imaging, also provides H-imaging
6	API	14 MeV neut. with assoc. α particles	(n,n' γ)	α in coincidence with γ	(D,T)	O, C, N	Long measuring time
7	NRA NES	ns pulses of white spectrum, or variable monoenergetic neutrons, $E_n < 7$ MeV	(n,n) resonances	Scattered or attenuated source neutrons	ns pulsed, (D,Be) white neutron spectrum	O, N, C H	Poor S/N, very difficult to get 3-D imaging
8	GRA	Monoenergetic γ -rays, 9.17 MeV	(γ,γ) resonance	Attenuation of photon beam	High current proton ($E_p < 2$ MeV), using ^{13}C (p, γ) reaction	N	Require very high current accelerator, complex mechanics for tomographic irradi.
9	Photo-Nuclear Activation	> 13 MeV Bremsstrahlung	(γ,n)	0.511 MeV from β^+ annihilation	High power electron linac	N	Requires extremely high dose rate, self absorption of signal (511 MeV) gamma-rays low efficiency, slow

*S/N = Signal to noise

A feature not commonly associated with nuclear techniques is the imaging capability. It is essential to the ability to distinguish with high selectivity an explosive or other

contraband from the surrounding benign substances. This is because the elements which are characteristic of explosives are present in suitcases in very large amounts. What differentiates explosives from benign materials is the concentration or density of these elements. Thus, to truly measure explosives, the amount of the key elements in a small volume must be determined. TNA and FNA techniques achieve this volume assay by image reconstruction techniques similar to the commonly known emission tomography. GRA inherently provides two dimensional information on the nitrogen distribution (sometimes called "nitrogram"). To get the necessary third dimension, a complete (and rather complicated) tomographic irradiation of the luggage is required. The photonuclear technique allows direct imaging by positron emission tomography. The PFNA technique views successive volumes (or voxels) in the interrogated object by following the neutron time of flight. The imaging capabilities and qualitative comments on the individual techniques are summarized in Table 2.

The various nuclear techniques for explosive detection were described in a recent publication¹. In the next section we will briefly review the status of the TNA and PFNA techniques. Very little reporting on the progress of the GRA technique is available in the open literature. It has been reported that the basic feasibility of the concept was demonstrated last year using a university accelerator. A more scalable demonstration is expected late in 1992 or early 1993. It was also reported that some progress has been made in one of the most critical parts of the GRA technique, namely the development of a very high current (factor 10 to 100 above what is achievable today) high beam quality proton accelerator.

3. STATUS OF TNA

Thermal Neutron Analysis (TNA) uses thermal neutrons as probes for non-invasive interrogation of suitcases for explosives. These neutrons are absorbed by the nuclei of the various substances inside the inspected object, which then emit prompt gamma rays uniquely identifying the elements from which they were emitted. Thus, specific substances are detected through their elemental structure. TNA technology was originally developed by SAIC in the 1970s for real time on-line assay of coal constituents such as sulfur and others. Following the Air India bombing attack in 1984, the FAA solicited R&D programs to develop explosive detection systems (EDS). A major R&D effort was undertaken by SAIC for the FAA towards the end of 1985 to develop a TNA based EDS. This project culminated in the TNA explosive detector prototypes being fielded and tested during 1987 and 1988. In 1989, in the wake of the Pan Am 103 disaster of December 1988, the FAA embarked on a limited deployment of improved TNA systems in major airports worldwide.

As implemented by SAIC, the TNA can detect variable amounts of all known types of military and commercial explosives regardless of shape or packaging. The TNA does not depend on operator skill or attention because the decision algorithm is fully automatic. In typical deployment, it can screen the full baggage load of a wide body or a 747 in about one hour. The device's performance level (PD -PFA) can be adjusted in the field to meet special alert situations, e.g., operating at a higher sensitivity level with the concomitant additional false alarms.

During the three years since first installation the fielded TNA machines (see Figure 2) have inspected more than 800,000 bags under a wide variety of operational

environments. TNA exhibited high detection capability (in excess of 90% for the designed threat level) together with a less than 10% alarm rate on ordinary luggage. At different sites, it has been operated at higher sensitivity levels in order to detect amounts of explosive much smaller than the amount for which it was originally designed. It has operated without failure or compromising performance in the humidity and the heat of

TABLE 2. Imaging capabilities of nuclear based detection techniques.

Name of Technique	Primary Signatures	Secondary Signatures	Imaging Capabilities	Comments
TNA	N	Cl, H	3-D, "Emission Tomography"	Limited view detectors improve spatial resolution, requires stronger source
FNA	O, C, N	H, Cl	3-D, "Emission Tomography"	Same as above
PFNA	O, C, N, Cl, Others	Metals, Si, Others	3-D, Direct	Imaging methods improve S/N* for the direct imaging, provides also H-imaging
GRA	N	-	2-D, Projection	Requires very high current proton accelerator
GRA	N	-	Pseudo 3-D, Multiple angle irradiation to achieve CT	As above; mechanically complex; longer measurement time
NRA	O, N, C	H	2-D	Poor S/N
NES	O, N, C	H	(3-D)	Poor S/N; complex; uncertain
Photonuclear Activation	N	-	(3-D) (Direct imaging)	Requires extremely high dose rate; self absorption of signal (.511 MeV) gamma-rays; low efficiency; slow

*S/N - Signal to noise

Miami and Saudi Arabia. TNA's operational availability has exceeded 99% over a total of 7 machine-years of operation, and there has not been a single case of a flight delayed because of TNA. TNA has been installed both in the baggage make up area, where it inspected transfer luggage, and in the ticketing area (concourse) where passengers' luggage was inspected prior to checking in. Most of the installations have been in the concourse, and that is where the largest number of bags have been screened.

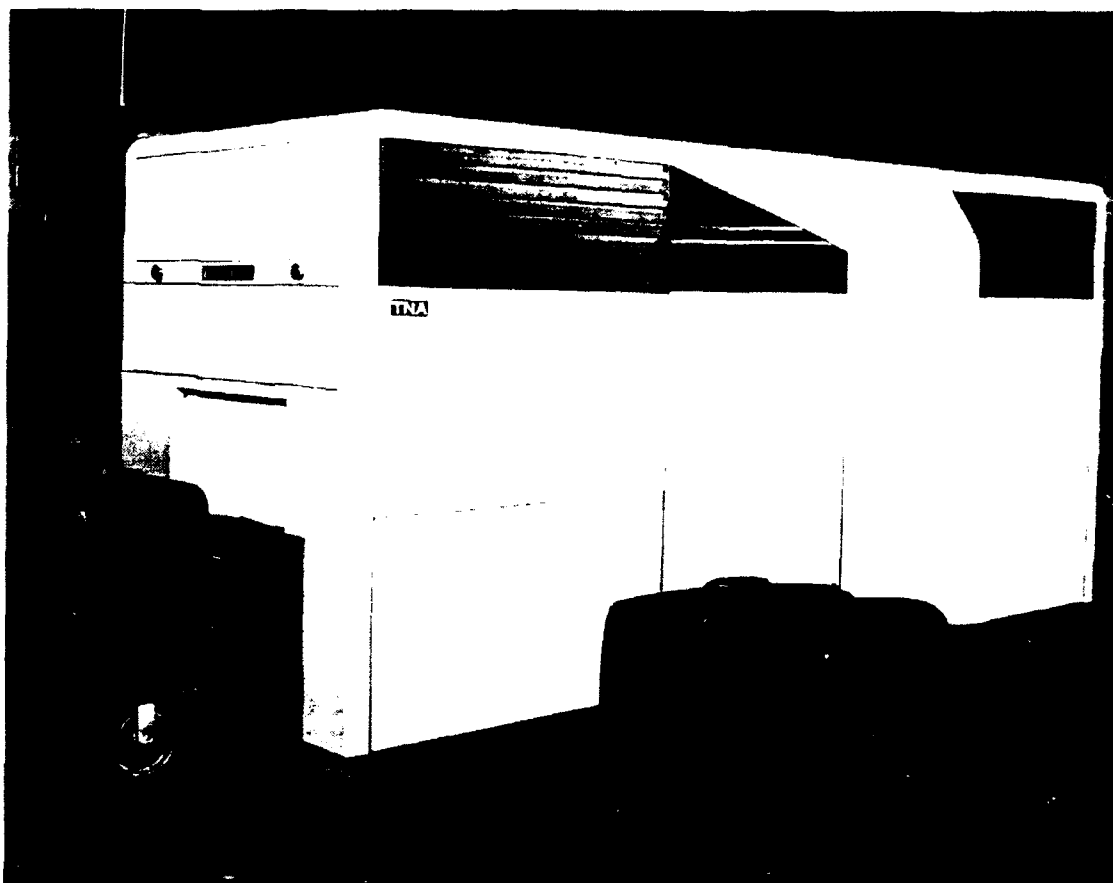


Figure 2. TNA Explosive Detection System

Over the past three years, the systems have been extensively tested by SAIC, the FAA, and third parties. Most test results are classified, but there are a few statements which have been released. From the unclassified summary of the National Research Council report, 1990: "Given the state of the art, a combination of sophisticated X-ray and a nuclear method such as thermal neutron analysis may offer the optimal approach for the detection of bulk explosives." And, in July of 1990, the TNA system was accepted as a part of the National Security Programme of the UK for use at Gatwick airport. For now, operation of the units at Gatwick and Dulles will continue, with two more units being installed in San Francisco International Airport in late 1992. Seven years since its

inception and three years since the first commercial TNA was installed, it is the only automatic explosive detection system ever developed and operationally successful.

4. STATUS OF THE PFNA TECHNOLOGY

The perceived need to detect ever smaller amounts of concealed explosives in luggage requires the development of a technique that is very sensitive and specific to most of the constituents of explosive. The nanosecond pulsed fast neutron analysis (PFNA) conceived in late 1987 by SAIC is such a technique. It probably fits the description of the "ultimate" explosive detection technology. This stems from the fact that it provides strong signals for all the key elements in explosives, namely: carbon, nitrogen, oxygen, chlorine and indirectly hydrogen. Other elements such as silicon, aluminum, iron, and other metals can also be detected. PFNA has a unique ability to directly determine the elemental concentrations in every volume element of the screened objects. The size of the basic interrogated volume can be as small as desirable, commensurate with the measurement time. Volumes as small as $5 \times 5 \times 5 \text{ cm}^3$ can be interrogated directly in a luggage. In a typical large luggage there are about 1000 such volume elements (voxels). The ability to measure directly such small volumes allows PFNA to detect very small explosives. The simultaneous determination of all or most of the elements present in explosives and benign materials makes PFNA on one hand, very specific, and on the other hand independent of the type of explosives, i.e., low or high nitrogen, low grade or high grade explosives, etc. Furthermore PFNA can detect the presence of incendiary materials or specialty explosives. Indeed, PFNA can be programmed to look for a large variety of materials, separately or combined, depending on their affinity (i.e., nuclear interaction cross-section) to fast neutrons and the strength of the emissions of the characteristic gamma rays.

In the current version of the nanosecond PFNA technique, neutrons are produced in an appropriate accelerator by the nuclear interaction of deuterons with a deuterium target. Most of the generated neutrons are produced in the forward direction due to nuclear kinematic constraints. The neutron beam is further defined by a mechanical collimator that removes the neutrons outside a desired angular opening. Thus the transverse size of the neutron beam, which defines the size of the interrogated area (or pixel) is determined by the mechanical (and variable, if so desired) collimator and the distance between the object and the location of the neutron target. The neutrons penetrate the object and interact with its elemental constituents to produce characteristic gamma rays. PFNA has the unique ability to determine where the interactions occur inside the object along the path of the neutrons. This feature is the result of the nanosecond pulsing of the deuterons and consequently the generated neutrons. The deuterons are accelerated in narrow, nanosecond wide bunches (pulses) and thus produce monoenergetic nanosecond bunches of neutrons. Knowing the time when the neutrons are produced, their velocity (i.e., energy) and the time at which they interact with the various elements emitting gamma rays (which move at the speed of light) tell us where the detected elements are. This technique, called Time of Flight (TOF), is well established and has been successfully used for many years in nuclear physics.

The PFNA operation requires the rastering of the neutron beam up and down while the screened object is moved perpendicularly on a conveyor. The collected gamma ray spectrum from each volume element is analyzed for the presence of various elements. If the elemental concentrations (or features based on them) in the specific volume and

possibly in nearby voxels, indicate the presence of explosives, or other designated target, the finding is indicated via the computer. The elemental distribution, probability of presence of an explosive, and other relevant information are shown in pseudo colors on the operator screen.

The principle of PFNA detection is discussed elsewhere². Examples of PFNA screening of a typical suitcase measured (using a single detector only) at the SAIC PFNA facility in Sunnyvale, California are shown in Figures 3 through 5. Figure 3 shows the oxygen, carbon and nitrogen distribution, as measured, in a suitcase filled with fabric. Only C and O, typical of fabric, are seen. Figure 4 shows the addition of a haircurler and small size Semtex cube. Much higher oxygen and nitrogen signals are seen, along with a higher carbon signal. Figure 5 shows the response of the system when a very thin Semtex sheet is added to one side of the fabric-loaded suitcase. Again, the localized increase in oxygen and nitrogen signals are quite obvious. Based on these signals various "explosive features" automatically detected the presence of the explosives.

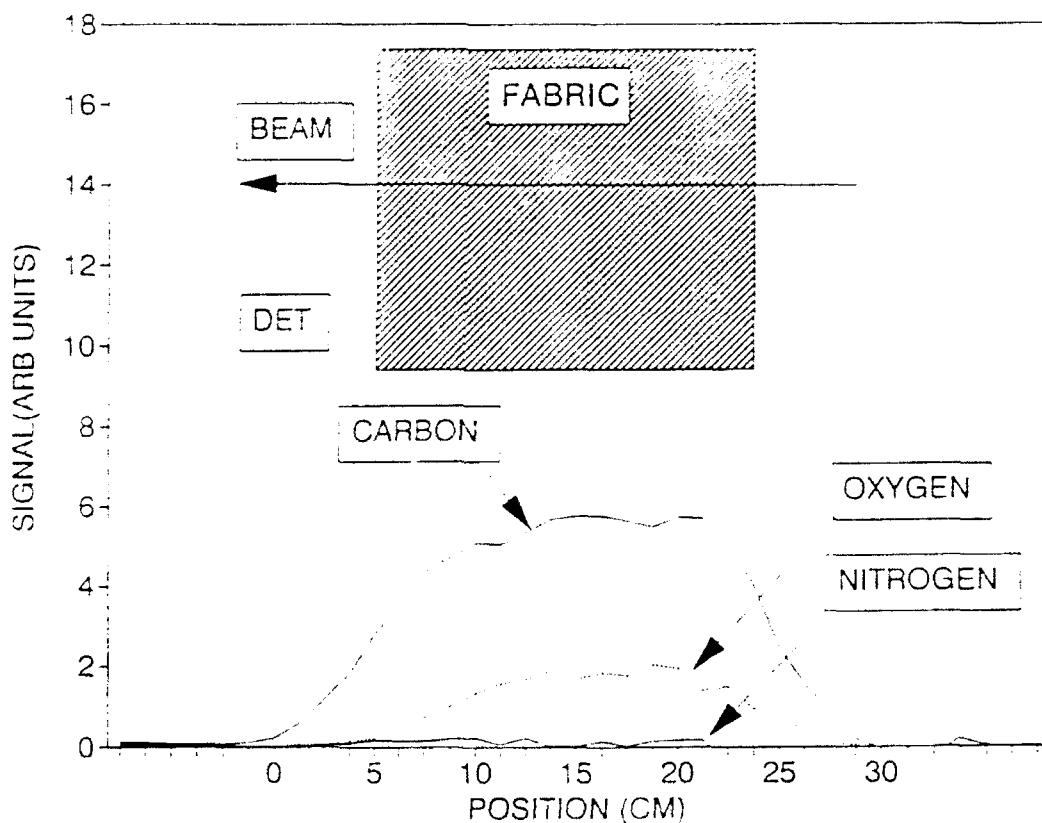


Figure 3. Gross elemental map (O, C, N) of a suitcase filled with fabric as measured by PFNA.

Extensive development and testing of PFNA to a more difficult task have been done. This task is the detection of explosive, contraband and other materials in large containers: air cargo containers, sea freight containers, and full trucks. This study demonstrated the unsurpassed capabilities of nanosecond PFNA for rapid and reliable non-intrusive examination of all sizes of objects with a wide variety of materials. Based on current support levels, it is anticipated that the first demonstration of PFNA to the interrogation for contraband of shipping containers, at an important port of entry in the U.S.A., will take place in early 1995.

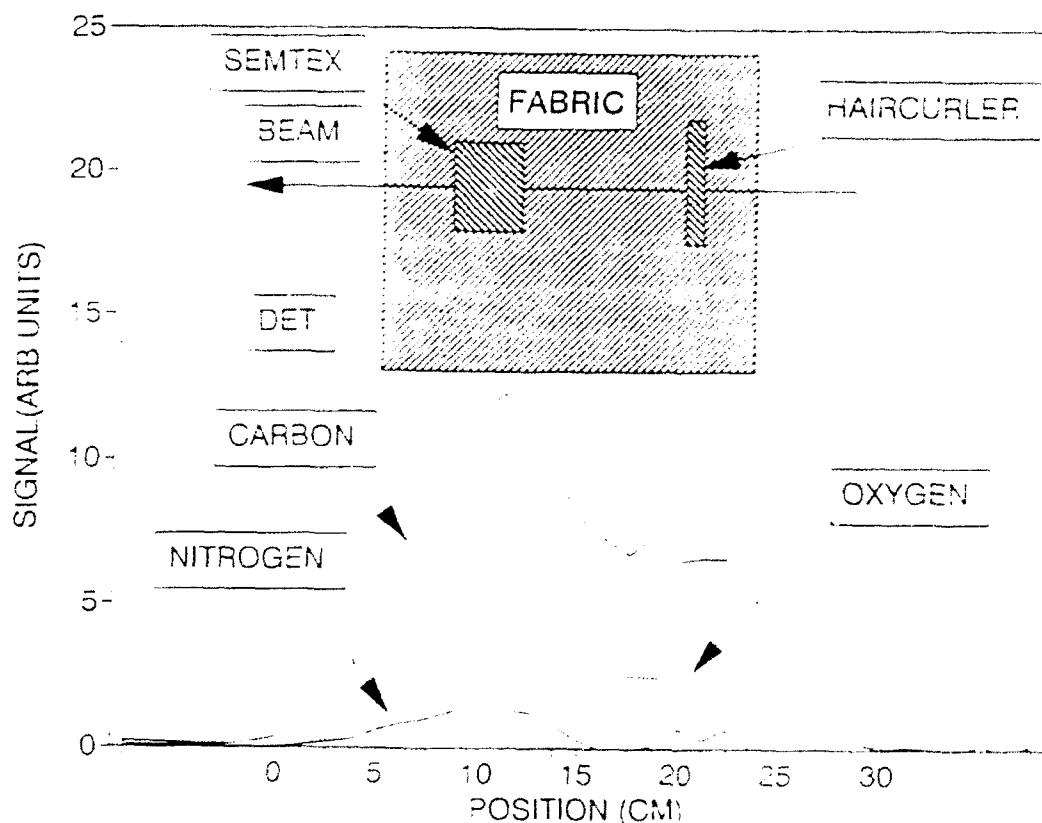


Figure 4. Gross elemental map (O, C, N) of a suitcase filled with fabric with a small amount of Semtex cube and a haircurler, as measured by PFNA.

5. THE CONCEPT OF SYSTEM OF SYSTEM

The basic idea behind the "system of systems" approach to security is nothing more than using the right tool for the right job. Individual screening devices (whether nuclear or non-nuclear) are used on different parts of the flow of people and materials onto the airplane, so that the strengths of one device compensate for the weakness of another. These devices are combined into a system by placing them in series or parallel, depending on whether

the goal is to improve detection rate or reduce false alarm rate. For example, a system with a high throughput (thousands of passengers per hour), high detection rate, but high false alarm rate (e.g., an automated passenger profiling process) may be used as an initial screening "device," followed by a slower (hundred passenger per hour), more expensive, but higher performance system (e.g., TNA or a CT system). Anything which cleared the first device would go directly to the aircraft; alarms from the first stage would be resolved by the next device. Such a combination would increase the overall throughput at excellent performance because the second system only needs to examine the false alarms from the first system.

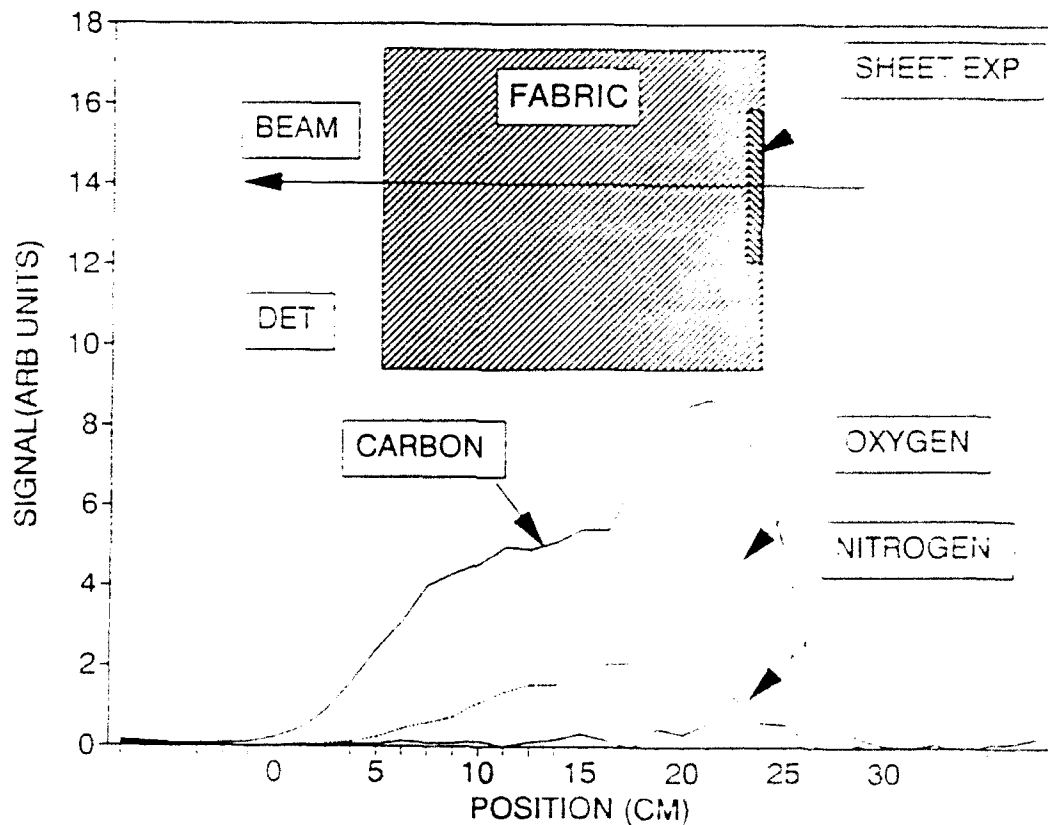


Figure 5. Gross elemental map (O, C, N) of a suitcase filled with fabric with a thin sheet of Semtex on one surface, as measured by PFNA.

The performance of a system of devices can be computed if the details of the individual devices and their connections are known. For each device, it is necessary to know the probability of detection of the target threat, the probability of false alarms on ordinary luggage, the throughput of the device, and the degree of correlation of error (both mis-detections and false alarms) with the other devices in the system. This last is particularly important and is often glossed over by assuming that different systems are independent. Two systems which are highly correlated (i.e., "make the same mistakes"), if combined in series might have reduced performance. This is unfortunately a

complicated area, and depends in detail on the types of correlation present in the system errors. In general, systems which use very different technologies are assumed to be statistically independent, and those which have similar physical principles will not be used in series. If devices are independent, then the probability of a system alarm (both systems agreeing) is $PD1 \times PD2$. The false alarm rate for the system would be similarly $PFA1 \times PFA2$.

Devices can also be combined in parallel to increase throughput by having multiple instances of the same device, where each inspected item only goes through one system. In this case, the PD and PFA for the system are just the respective rates for the individual system, but the throughput is increased. Devices may also be combined in parallel to improve detection probability, in which case each item to be inspect must go through both systems. In this case, the item is only cleared if both systems agree that it is clear. The system PD would be $PD1 + PD2 - PD1 \times PD2$, and the false alarm rates would combine similarly and hence be higher. Parallel combinations are used to improve detection rate at the cost of additional false alarms; series combinations are used to reduce the false alarm rate at the cost of reduced detection rate. Often, tiered systems are used which have both parallel and series stages.

In order to correctly "trade off" various devices to build an optimal system, detailed, objective data on the performance of the system must be available. This can be obtained for automated systems, which can be objectively tested, but is not available for a large number of the proposed systems (e.g., those involving humans or dogs). In addition, the covariances between different devices can only be measured in practice. To date, extensive tests have been done with TNA and limited tests with automated X-ray, backscatter X-ray, and CT systems. In several cases, there are significant correlations which can be taken advantage of. Specifically, the weak detection areas of some devices can be compensated by the "best" detection areas of other devices. The classification of test results for the various explosive detection devices has added a difficulty in doing system level tradeoffs. Quite rightly, the weak and strong points of different devices are protected. However, this means that demonstrations of the effectiveness of systems of devices must generally be done using "made up" data.

Several studies have been done discussing the effectiveness of systems of hypothetical devices^{3,4}. Table 3 summarizes the parameters used to describe several different devices that might be combined into a system. It should be noted that the numbers given in Table 3 are estimates for discussion only, and represent a single operating point. The systems discussed can be operated at a number of different points (e.g., higher PD and higher PFA, or lower PD and lower PFA), but the performance given in the table represents some "knee" point in the tradeoff curve. Deviation from such a point results in a great deterioration of one parameter or other. Most of the systems in the table are self explanatory. The "Focused Hand Search" is the search that is done by trained personnel once one of the automated systems has identified a small area of the bag to be inspected. The TNA with X-Ray (known as XENIS) is the combination of Thermal Neutron Analysis with a standard X-ray system in an integrated manner, taking advantage of the covariances between the units.

Figure 6 shows a sample system of systems that might be used at an airport. Some portion of the passengers (say 10%) are randomly selected to go straight to the XENIS system for inspection. All others go through a profiling procedure, and those that aren't cleared are also sent to the XENIS system. This demonstrates a system with both parallel

and serial aspects. There are 5 profiling stations, 1 XENIS, and 3 hand search stations to meet the bag throughput requirements. Combining the probabilities of detection and false alarm in the appropriate manner gives for this system an expected probability of detection of about 82% and a false alarm rate of 1 bag in 25000.

Table 3
Parameter Estimates Used in Initial Analyses

Inspection Technique	Input P_d	Input P_{fa}	Time Per Unit
Automatic Profile	.750	.200	30 seconds per passenger
Manual Profile	.950	.100	300 seconds per passenger
Focused Hand Search	.999	.001	200 seconds per bag
Unfocused Hand Search	.950	.001	300 seconds per bag
TNA with X-Ray (XENIS)	.900	.200	6 seconds per bag
Vapor Detector	.600	.100	30 seconds per bag
Enhanced X-ray	.750	.200	20 seconds per bag

Key: P_d : Probability of detection
 P_{fa} : Probability of false alarm

The system as shown can also be evaluated by stochastic modeling techniques to assess overall throughput, queue sizes, and the like. Passengers for flights are assumed to show up over the course of 3 hours before a flight, with a triangular distribution. When this model was evaluated, the system shown in Figure 6 could process 1200 passengers in a little over 3 hours. The largest number of passengers in the system (queued up at the various stations) was approximately 70. Some sensitivity studies were done; for example, reducing the number of profiling stations led to a near doubling of the maximum number of passengers in the system. These studies are very valuable when trying to trade off the limited space at an airport against the need for speedy security.

In summary, finding the right mix of devices for an airport requires accurate knowledge of the performance of available devices (both separate and in combination), detailed information about the operation of the airport, and a clear understanding of the level of security required. Once those items are obtained, tools exist for finding the optimal means of satisfying those goals. The optimal solution will almost certainly use a collection of devices rather than just one device. Unfortunately, the lower capital cost, non-automated systems (such as dogs and X-rays) are very difficult to objectively characterize, and their use in explosive detection systems is often an act of faith rather than science. Similarly, it seems that the only politically palatable specification for security

is "perfect"--100% detection and 0% false alarms. That cannot be met by any combination of systems given in the table or elsewhere.

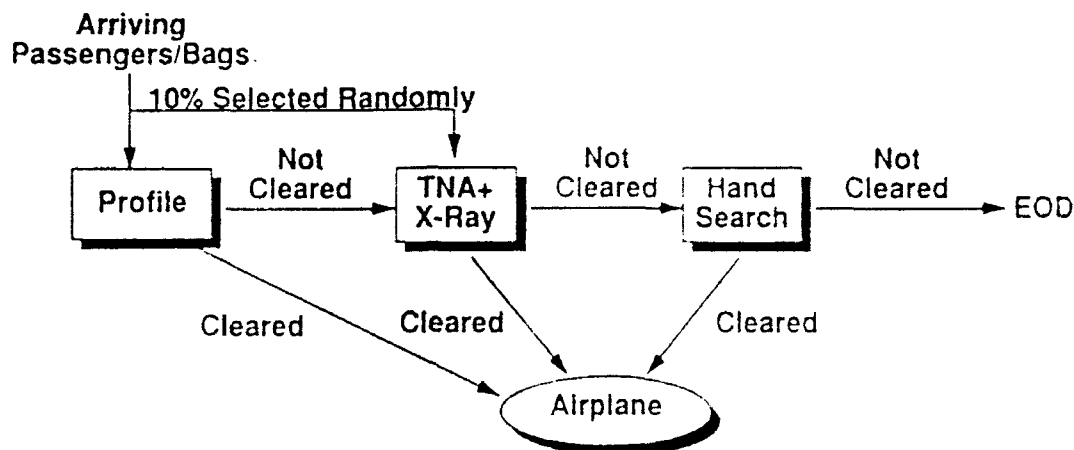


Figure 6. EDS configuration based on Gatwick Airport.

6. CONCLUSION

Unlike a few years ago, the security classification of important test results has limited the details possible in this review. The development of explosive detection systems has split into two paths: the long term stretched research into improved nuclear-based explosive detection systems, and the study of improved conventional systems which are considered more acceptable to the user. There are several promising high performance systems being pursued, including TNA, GRA and PFNA, but all are directed at the long term. There has been continued incremental success in all of these areas.

NOTES

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²Sawa, P. and Gozani, T. "PFNA Technique for the Detection of Explosives," *Proceedings of the First International Symposium on Explosive Detection Technology*, pp. 91-106, November 13-15, 1991, FAA Technical Center, Atlantic City International Airport, February 1992.

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EXPLOSIVES DETECTION - THE CASE FOR MAGNETIC RESONANCE

J. Derwin King
Armando De Los Santos
Southwest Research Institute
P.O. Box 28510
San Antonio, Texas 78228-0510, U.S.A

ABSTRACT. Distinctive properties of the hydrogen transient magnetic resonance (HTNMR) response from explosives provide a basis for rapid, selective and sensitive detection of these materials concealed in parcels, letters and airline baggage. Most common high energy and commercial nitrogenous explosives as well as many which do not contain nitrogen, are detectable. Full scale inspection systems based on this technology have demonstrated performance comparable to the best reported for any other method.

The theory of HTNMR and related radio frequency resonance methods are briefly reviewed and a full scale inspection system is discussed. MR data on many explosives are presented and compared to common materials found in baggage and other items. The potential to further increase the useful sensitivity and the inspection rate are analyzed and the possibilities for reducing present limitations are discussed.

1. Introduction

Despite extensive efforts over the last two decades only a few viable and generally useful explosives detection technologies have been identified. These include the nuclear radiation (neutron and gamma ray) methods, vapor detection, x-rays, and the radio frequency resonance absorption (RRAS) methods which includes nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR) and electron spin resonance (ESR). A limited number of other methods such as microwave and acoustics, have utility for a few specialized applications. The four primary technologies can be useful for detecting explosives in a variety of concealments and all provide at least some capability to cope with the multitude of different materials and items encountered in practical inspection scenarios. Each of these technologies has particular advantages and limitations.

Any acceptable explosives detection system (EDS) must provide a safe and effective inspection of items of concern. To minimize nuisance alarms it must provide selectivity to explosives and must also exhibit adequate sensitivity to rapidly detect explosives in quantities that pose a threat to persons and equipment. The EDS must rapidly and reliably distinguish between explosives and non-explosives and should provide detection independent of explosive configuration and distribution. It should also be tolerant of the non-explosives contents and the structures of items being inspected. Automated inspection is desirable and the apparatus should not pose a health hazard to the public nor the operators nor damage items or contents. It should be reliable, friendly and affordable in initial cost, installation and operation. Radio Frequency Resonant

Absorption Spectroscopy (RRAS) techniques were considered early in the efforts to provide an acceptable solution to this inspection problem and these methods still provide features and capabilities that are largely unmatched by other technologies. One of these techniques, hydrogen transient nuclear magnetic resonance (HTNMR) has been found to be particularly useful for the practical detection of most explosives concealed in letters, parcels and baggage^{1,17} while ESR is particularly useful for detecting black powder¹ and a few other materials. NQR can detect several nitrogen and chlorine based explosives.^{17, 19}

An approach common to some EDS technologies is to provide selectivity to explosives by basing the detection on sensitivity to one or more of the elemental constituents. For many of the common explosives this includes hydrogen, carbon, oxygen and nitrogen. A detector sensitive to any one of these could theoretically detect explosives. However, unless some unique feature that is characteristic of explosives is available in the detected response, the system will be plagued with false alarms since these same elements are common to many natural and man-made materials. Substantial efforts have been made with varying degrees of success, to identify and utilize means that would provide better specificity for each of the basic detection methods. Having this capability has been particularly pertinent to the success of HTNMR which in elementary form detects all the hydrogen in items being inspected. Since almost all common materials contain hydrogen in one form or another, the selectivity to explosives must come from features in the hydrogen MR response that allows these materials to be distinguished from non-explosives. Fortunately, explosives exhibit HTNMR signal relaxation properties that are different from most other common materials. This feature is absolutely essential to the successful application of this method for inspection since the vast majority of non-metallic materials contain hydrogen and produce strong hydrogen NMR signals. Additionally selectivity is provided in HTNMR by the ¹H-NMR to ¹⁴N-NQR level crossing effect.²⁻¹⁸ This provides useful selective signature data for some explosives and is also effective in drastically reducing the detection time for these. The unique HTNMR signal relaxation properties have been found to be characteristic of almost all explosives of concern. This includes the high energy military explosives as well as the more common commercial explosives such as dynamites and water gels used in civilian construction, excavation and mining activities.

In addition to specificity for explosives, a successful EDS must also have sufficient useful sensitivity to detect the threat quantities of concern. The useful sensitivity is not just the basic, idealized, theoretical capability even though this does define the starting point that sets the lower limit on the quantity of explosives that can be detected using an idealized apparatus and test conditions. For any of the technologies the sensitivity that can be achieved in practice and the probability of detection, are greatly affected by the background "clutter" from the non-explosives materials and other sources of interference that are present. The basic sensitivity of HTNMR, as shown later, is very high. For items that can be inspected by this technology the detection sensitivity achieved to date in practice, in the real world, with a full scale inspection system is comparable to the best reported for any other technology^{12, 17} but is still below the theoretical limit. There is room for improvement by advances in instrumentation techniques to better reduce effects of background interference and clutter.

HTNMR, like the other RRAS methods, does not use nuclear radiation, radioactive sources, x-rays nor any other form of ionizing radiation. Instead detection is accomplished through magnetic and electromagnetic fields used to sense the hydrogen contained within the materials of the item to be inspected. By analyses and processing of this total hydrogen NMR signal, any contribution to the response produced by hydrogen in explosives can be separated from that produced by the hydrogen in most other materials. Through this procedure the HTNMR response

has been found useful for rapidly and selectively detecting nitroglycerine-based dynamites, water gel explosives, C-4 (plastic) explosives, RDX, TNT, PETN, smokeless powder and most other high-energy and commercial explosives and propellants. Results^{2,12} of several thousand tests have demonstrated the general suitability of the HTNMR method for baggage, letter mail, and parcel inspection and have shown a high detection probability and a low rate of false alarms. The small percentage of items that could not be effectively inspected were automatically identified by the apparatus. Work currently underway is expected to extend the capability to inspect most items, and to extend the detection capability to other classes of explosives and to minimize effects of the magnetic field.

2. HTNMR Properties of Materials

Figure 1 illustrates the typical range of HTNMR relaxation time constants for most solid, bulk explosives and for common, non-explosives materials likely to be encountered in items likely to be inspected by an EDS. At the indicated measurement frequency, near 3.0 MHz, explosives are well separated in either T_1 or T_2 (see Appendix A) from other materials that are usually found in parcels, letters and baggage.

Emulsions have properties more like liquids and additional features in the HTNMR EDS are needed to selectively detect these materials as well as other liquid explosives. Means to implement these features have been identified. While most of the interest has been in hydrogen-nitrogen based explosives, limited measurements have shown similar HTNMR relaxation time characteristics for hydrogen-chlorine based explosives.

3. Selectivity of HTNMR

An HTNMR inspection apparatus processes the total hydrogen signal to isolate and alarm on any detectable signal component having the long T_1 and short T_2 characteristics of explosives. The degree of perfection in the capability of the processing hardware and software sets the limit of the smallest amount of explosives which may be detected while keeping the nuisance alarm level within acceptable bounds.

4. Sensitivity

The basic sensitivity of HTNMR is a measure of the smallest quantity of the material of interest that may be theoretically detected. This is set by the signal-to-noise ratio that the material produces when tested by the HTNMR apparatus. From Andrew²¹ this may be calculated using

$$\frac{V_s}{V_n} = \left(\frac{y \xi N \gamma I (I+1) \hbar^2}{48 k T} \right) \left(\frac{4 V_c Q \nu_o^3}{k T B F} \right)^{1/2} \quad (1)$$

where

V_s/V_n = Voltage signal-to-noise ratio

y = Instrumentation factor ≈ 1

ξ = filling factor i.e. volume of sample/volume of sensor coil

N = volume density of nuclei to be detected

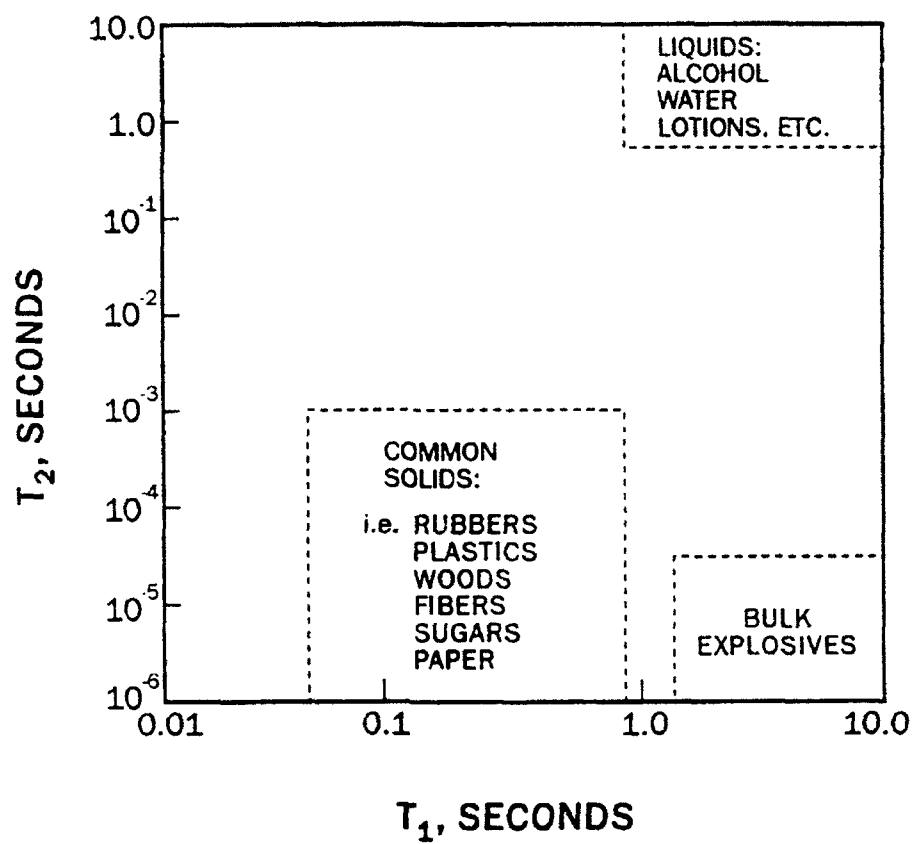


FIGURE 1. TYPICAL 3.0 MHZ RELAXATION TIME CONSTANTS FOR EXPLOSIVES AND COMMON NON-EXPLOSIVE MATERIALS

γ = nuclear gyromagnetic ratio
 I = spin number
 h = Planck's constant
 k = Boltzmann's constant
 T = Temperature, K
 Q = Quality factor of sensor coil
 V_c = Volume of sensor coil, cm^3
 ν_0 = Resonant frequency for nuclei of interest, Hz
 B = Detector Bandwidth, Hz
 F = Noise voltage factor of detector

For hydrogen nuclei, (1) may be reduced to

$$(V_s/V_n) = (4.35 \gamma N_h \times 10^{-30}) (Q V_c^3/B F V_c)^{1/2} \quad (2)$$

where

N_h = Total number of hydrogen nuclei in sample under test
 $= M_s (n/MW) (6.02 \times 10^{23})$
 M_s = weight of sample, grams
 n = number of hydrogen nuclei per molecule of sample
 MW = molecular weight of sample

From (2) it is apparent the signal-to-noise increases directly with the number of nuclei in the HTNMR sensor. It also increases by $\nu_0^{3/2}$ as the resonant frequency is increased by increasing the magnetic field intensity. The V_s/V_n improves as a square root function of the Q of the sensor coil and similarly decreases as the detector bandwidth, volume of the sensor coil and noise factor of the detector are increased. Thus the minimum quantity that can be detected is affected by the density of the target nuclei in the material of interest and by the sensor parameters. Choices of Q and B are limited by requirements imposed by the relaxation time parameters of the material to be detected and F is set by the noise figure of available amplifier devices. The sensor volume, V_c must be adequate to accommodate the item to be examined but the smaller this can be made, the better the signal-to-noise for a given quantity of material. To examine the basic sensitivity of HTNMR for inspecting large parcels consider a sensor volume of $2 \times 10^5 \text{ cm}^3$ and HMT as the target material to be detected. This material is not an explosive but has HTNMR characteristics somewhat similar to several explosives and an M_h of $5.16 \times 10^{22}/\text{gm}$. The Q and B are optimized for this material, ν_0 is selected to be 3.0 MHz and F is 1.1 -- a noise figure of about 0.8 dB. Using these parameters a voltage signal-to-noise ratio of 21.6 (or 26.7 dB) is calculated for 1 Kg of this material. V_s/V_n of 2.0 (or 6 dB) is calculated for 92.5 grams. While these figures do not represent what has been realized in practice they do show the high sensitivity potential of the HTNMR technique. How close this performance can be realized in a practical inspection system depends on the perfection of the instrumentation hardware and processing algorithms. The minimum amount that can be detected is also highly dependent on the effective volume of the sensor. The total available volume can be divided into several regions to reduce the effective volume for each test and thereby improve sensitivity.

The sensitivity of HTNMR is not affected by the distribution of the sample within the sensor region, only by the total of the material. Thus clumping of the explosive into a small volume or spreading it into a thin sheet does not affect the detectability.

5. Application to Explosives Detection

An explosives detection system must rapidly inspect all items of interest, in "as received" condition, without causing damage and must reliably detect all explosives in quantities of concern regardless of the configuration and distribution and must produce a minimum of false alarms. These criteria can be realized only if the apparatus responds to a signature that is specific to explosives and which is not encountered in other materials commonly found in quantity in the items being inspected. In addition the inspection apparatus must have sufficient sensitivity to produce a signal level from the smallest quantity of explosive of interest that is well above both the apparatus noise level and any clutter level which results from other contents of the item. This condition must hold even in the presence of any degrading effects of the item. These capabilities have been realized in magnetic resonance inspection apparatus through use of rather simple and un-sophisticated NMR techniques compared to those that are now available and common in analytical and imaging laboratories. However, these simple methods do work quite well in the practical environment encountered in many inspection applications.

In a full scale HTNMR inspection system the inspected items are conveyed through a polarizing magnetic field of selected intensity and then into the inspection magnet. The item pauses for less than one (1) second in the inspection magnet while the HTNMR data required for inspection is acquired. The bag remains stationary for a short time while the computer processes the data and indicates "alarm", "pass" or "inadequate test". In a system previously implemented the inspection rate was 10 to 12 items per minute but this can potentially be increased to near 30 per minute.

The HTNMR data required for processing is obtained in a set of multiple pulse sequences. These data allow HTNMR signals from materials having the characteristics of explosives to be recognized in the presence of the (typically) much larger HTNMR signals from the normal contents. The processing algorithms are such that effects of the items and contents on the magnetic field intensity and homogeneity and on the sensor coil resonance characteristics are minimized. The result is that quantities of explosives of concern for many applications can be detected with a high probability while potential false alarms from much greater quantities of non-explosive materials are greatly suppressed. This is accomplished in essentially one test sequence without benefit of any signal averaging by making use of the T_1 , T_2 and $^1\text{H} - ^{14}\text{N}$ level crossing characteristics of the HTNMR signals.

6. Enhanced Performance

Improvements in several areas could make magnetic resonance technology even more capable of meeting the needs for an operational explosive detection. One of these is operation at lower magnetic field intensities to eliminate the need to remove recorded magnetic media prior to inspection and to enhance the capability to effectively inspect all items.

Originally the HTNMR work was primarily directed toward detection of bulk (solid) explosives but developments over the past several years have shown the need to also detect liquid and emulsion type explosives. Means for adding this capability are known.

Incorporation of known improvements in the apparatus and processing algorithms to increase specificity to explosives could produce substantial reduction in the false alarm potential and extend the capability to detect quantities of explosives comparable to the basic sensitivity limit. Increased tolerance for effects of the item structure and contents could also potentially improve the detection probability and reduce the false alarm rates.

To be acceptable any enhancements must be achieved without substantially increasing the

inspection time, the magnetic field intensity, or the size, weight and cost of the apparatus. The improvements must also cause no damage to the bag, be accomplished with acceptable parcel handling practices, and be tolerant of the effects of the item and contents on the RF and magnetic field homogeneities and intensities. Current work of the authors is directed toward practical achievement of enhanced capabilities in most of the identified areas.

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APPENDIX A BASIC NMR METHOD

Nuclear magnetic resonance is generated by interactions between the magnetic moment of atomic nuclei in materials being inspected and an externally applied magnetic field. The frequency of this resonance is typically in the high radiofrequency range and is dependent upon the intensity of the applied magnetic field and the specie of the nuclei. In the case of hydrogen the resonant frequency, f , is related to the magnetic flux density, H , by

$$f = 42.57 H \quad (1)$$

where

f = frequency, MHz

H = Magnetic flux density, T (Tesla)

The choice of the magnetic field intensity used for NMR is somewhat arbitrary but is based on trade offs between the improved sensitivity available at high fields and the greater size, weight and cost of the required magnet structures, and the increased potential for damage to items being inspected as the flux density is increased. For explosives detection the field intensity is made as low as possible consistent with adequate sensitivity to rapidly detect the quantities of concern.

Figure A-1 illustrates the basic NMR detection concept. The item being inspected is located in a magnetic field of selected intensity, H , and tested with an electromagnetic field having a frequency, f , corresponding to the nuclear resonance. In the transient mode of operation as used for explosives detection the electromagnetic field is applied in short pulses (RF bursts) of controlled width and amplitude. Detected NMR responses are in the form of transient radio frequency signals emitted by the excited nuclei following the burst of transmitted energy. The frequency of the emitted NMR signal is that for nuclear resonance in the applied magnetic field, H , and the peak amplitude is proportional to the number of nuclei contributing to the response. The transient, free induction decay (FID), signal following a single transmitter pulse decreases in amplitude at a rate which, in a homogeneous magnetic field, is dependent upon the spin-spin time constant, T_2 . This time constant is characteristic of the molecular structure and the state of the sample material as is the spin-lattice time constant, T_1 , which sets the time required to detect an NMR response and the rate at which NMR tests may be repeated without signal degradation. Transient NMR for explosives detection makes use of multiple transmitted pulses of appropriate energy and spacing to aid in achieving selectivity to the T_1 and T_2 relaxation time constants and to the ^1H - ^{14}N cross coupling properties of the explosives.

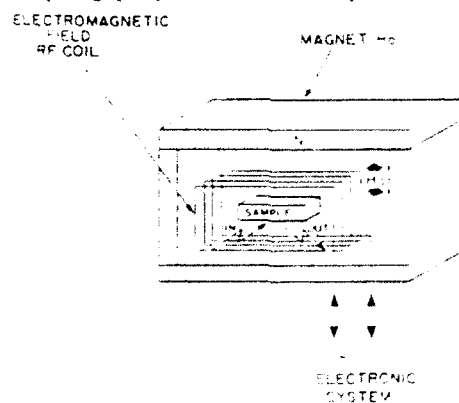


FIGURE A-1. BASIC NMR DETECTION CONCEPT

EXPLOSIVES DETECTION BY ^{14}N PURE NQR*

M. L. Buess*, A. N. Garroway, J. B. Miller, and J. P. Yesinowski
Code 6122, Chemistry Division, Naval Research Laboratory,
Washington, DC 20375-5000, USA
*Sachs Freeman Associates, Landover MD 20785, USA

ABSTRACT. Pure ^{14}N nuclear quadrupolar resonance (NQR) is quite promising as a method for detecting explosives such as RDX in quantities which are a threat to aircraft security. We have constructed a proof-of-concept NQR explosives detector which interrogates an active volume of 300 liters in 6 seconds. We first outline the basics of the NQR approach, highlighting strengths and weaknesses, and then present representative results from our RDX detection system.

1. Introduction

The goal of this project is to construct and evaluate a full size, proof-of-concept nuclear quadrupolar resonance (NQR) detector of explosives and, further, to explore NQR techniques in the laboratory in sufficient detail in order to provide realistic design criteria for an NQR prototype fieldable at an airport. General guidelines are the detection of sub-kilogram quantities of explosives within 6 seconds with a detection probability of 99% and false alarm rate no greater than 1% for RDX. We concentrate on RDX-based explosives since, on the basis of published data [1], RDX is (one of) the most favorable explosives to detect by NQR. Moreover, RDX is a component in many of the more common military explosives. Our primary focus is a detector for checked or carry-on baggage, but we also consider NQR for potential application to examining people. For a suitcase size detector, the goal is detection of sub-kilogram quantities of explosives, with a lower detectable quantity for people scanning.

We point out that some narcotics can also be detected by NQR techniques: nitrogen is present in cocaine and heroin, while $^{35,37}\text{Cl}$ NQR may be appropriate for their respective hydrochloride forms. The present work does not consider narcotics in detail.

2. Background

NQR is a particularly attractive approach to the problem of explosives detection, as the ^{14}N NQR absorption frequencies from crystalline materials are virtually unique. Hence,

by looking for the nitrogen signal at, say, the NQR frequency of RDX, *only* those nitrogens in RDX will be detected. Therefore we do not expect that systematic false alarms, due to 'interferences', will be a problem with an NQR explosives detector. A literature search of the 10,000 compounds that have been examined by NQR fails to show any other NQR resonances sufficiently near to that of RDX that would constitute an interference. This specificity feature should be contrasted with nuclear-based techniques, for which *all* nitrogen cross-sections are the same, independent of the chemical composition of the material.

NQR would determine the presence of other classes of explosives (e.g., PETN) by examination at the corresponding NQR frequency for PETN. In principle, such examination could be performed essentially simultaneously with the RDX inspection, but implementation of such technical details is not a major goal of this present project.

'Pure NQR' is the examination of nuclei with nuclear quadrupolar moments in the absence of a static magnetic field. Hence, in addition to its specificity, a second advantage of NQR is that no magnet is required, in contrast to nuclear magnetic resonance (NMR) methods. Hence damage to magnetically recorded material is avoided in (pure) NQR; there is no exposure of large, static magnetic fields to personnel; and, since a magnet is not required, the costs are lower than for an NMR system. Furthermore, NQR uses non-ionizing (RF) radiation whereas nuclear techniques employ ionizing radiation.

There are some inherently unattractive features of NQR which must be addressed for a successful NQR explosives detector. NQR signals are weak and are generally below the level determined by the random electrical noise in the radiofrequency (RF) coil which detects the signal. The signal-to-noise ratio is increased by repeating the experiment as rapidly as possible and adding up the results: the signal-to-noise ratio improves by the square root of the number of repetitions. The maximum rate at which the experiment can be repeated is generally determined by the spin-lattice relaxation time, T_1 , typically in the range 10 - 1000 ms for ^{14}N NQR. Hence, under a conventional approach, the maximum NQR signal, corresponding to the equilibrium magnetization, is generated when the experiment is repeated at time intervals greater or equal to T_1 . We employ a particular RF pulse sequence, a strong off-resonance comb (SORC) of pulses [2,3], which produces an NQR signal about equal to one-half of the equilibrium magnetization but at intervals comparable to the spin-spin relaxation time, T_2 , on the order of 1-10 ms. Thus, in a given total scan time, we gain a factor of about $1/2(T_1/T_2)$ in signal-to-noise ratio over conventional approaches.

We are also examining the potential of NQR as a people scanner. A very intriguing type of surface coil is the 'meanderline', for which the RF currents meander back and forth in a regular linear array of conductors [4]. We had earlier examined the meanderline RF coil and demonstrated for the first time its use in NQR [3]. A particular advantage of the meanderline is that the RF field intensity falls off very rapidly away from the surface of the coil. We anticipate that an NQR people scanner could be constructed with a meanderline that has sufficient sensitivity to see an explosive on the human body, but which does not deposit significant RF power into the body.

3. Implementation and Results

Figure 1 shows part of a full scale proof-of-concept NQR explosives detector for airline baggage that has been designed and built at the Naval Research Laboratory. The 300-liter radio frequency (RF) coil sits inside a screened cage. To the left of the cage are the RF amplifier and receiver; the PC-based controller and data system are at the far left. In a commercially built system the electronics can be constructed more compactly than in this laboratory version.

The contents of the suitcase in Figure 1 illustrate some advantages of NQR for explosives detection. No large magnetic field is required, so magnetic media (e.g., disks and credit cards) are not corrupted. The presence of ferromagnetic material (steel, electric shavers) does not interfere with the inspection. In our experience, electronics can be safely inspected. Due to the high chemical specificity of NQR, other nitrogenous materials, such as nylon, polyurethane or nitrile rubber, do not produce an interfering signal.

We have not yet optimized either the hardware or the details of the NQR pulse sequence. We elected to freeze the implementation of the NQR explosives detector at a reasonable, though not optimal, operating condition and perform a series of benchmark tests to evaluate performance under laboratory conditions. Rather than challenging the system with thousands of different bags, each with different contents, we employed only one arbitrary suitcase geometry: no attempt was made here to look for systematic variations. Table 1 presents these abbreviated test results: these results indicate the capability of the NRL NQR explosives detector, but do not represent a definitive test of the technology or the system. These data are for the RDX NQR resonance at 5.2 MHz.

In Table 1 the 'Alarm/No Alarm' determination is based on a preset threshold value, set to give a 1% false alarm rate for the empty detector. The detection rate is reported as 99+%; no missed detections were recorded for these tests. If the noise distribution were indeed strictly Gaussian, a detection rate of 99.99% would be *anticipated* from the signal-to-noise ratio under these conditions.

The performance of the detection system can be better understood by examining the distributions (Figure 2) of the actual intensities of the NQR signals under these four test situations: (a) empty; (b) RDX only; (c) suitcase and contents; (d) suitcase, contents and RDX. For each condition, the 6-second scan was repeated for either 400 or 1000 trials. For clarity, the areas of each distribution are normalized. Also shown is the threshold value, set to produce a 1% false alarm rate for the empty detector. This overall test examines only the random noise contribution to the detector: the variations seen in signal intensity in Figure 2 reflect primarily the Johnson noise in the coil and preamplifier front end. Some further systematic 'noise' may be anticipated on examination of a large set of differing bags and contents.

Table 1

Conditions:

Scan time (data taking)	6 seconds
Quantity of RDX explosive	Sub-kilogram
Suitcase and contents*	35 pounds (16 kg)
	2 ft ³ (60 liters)
NQR detector size	10 ft ³ (300 liters)

Summary of Results:

<i>Specimen</i>	<i>Number of Trials</i>	<i>Alarm</i>	<i>No Alarm</i>	<i>Detection Rate</i>	<i>False Alarm Rate</i>
Empty	1000	10	990	-	1.0%
RDX	400	400	0	99+ %	-
Suitcase + contents*	400	3	397	-	0.75%
Suitcase + contents* + RDX	400	400	0	99+ %	-

* Two small hardsided nylon lined overnight bags were used in place of a single large suitcase. Contents were:

2 hardcover books	electric shaver	steel hammer	NaNO ₂ (2 kg)
rubber soled shoes	computer diskettes	aerosol can	1-liter Perrier water
1-liter methanol	nylon fishing line	flashlight	2 horseshoe magnets (125 g)
hooded sweatshirt	electronic calculator	polyurethane (400g)	
2 sweaters (75% wool; 50% ramie)		man's windbreaker (polyester/cotton)	

In Figure 2 note that the signal profile for the empty detector (a) is substantially the same as for the suitcase and contents (c): there are *no* interfering NQR signals from benign baggage contents. Further note that the signal intensity distribution for RDX alone (b) is comparable to the response for the RDX *with* the suitcase and contents (d): the suitcase and contents do not mask the RDX signal. The bag contains 2 kg of sodium nitrite; while this material gives a very strong NQR signal at around 3.6 and 4.6 MHz, its resonances are quite far away from that of RDX and so do not contribute in the region of interest. Finally, the substantial separation between the NQR signal response of the 'clean' and 'dirty' bags provides a very high detection probability and low false alarm rate.

Figure 3 presents data for detection of RDX based on the 3.4 MHz NQR resonance line in RDX. In general, the signal-to-noise ratio depends approximately on the 3/2 power of the resonance frequency, and so the 3.4 MHz results would be expected to have a signal-to-noise ratio reduced by a factor of 1.9 from the 5.2 MHz results of Figure 2, for the same quantity of explosives. However, recent improvements to the system have increased the overall signal-to-noise ratio, so that the detectability at 3.4 MHz is essentially the same as that obtained from the earlier data (Figure 2) at 5.2 MHz. Figure 3a presents a series of 400 sequential 6-second scans with and without the presences of RDX. Note that the average signal intensity S_0 of the RDX 'bomb' is substantially

greater than the standard deviation σ_b of the noise, so that the threshold level can be set to provide excellent detectability with a very low false alarm rate.

It should be emphasized that the noise encountered in the NQR detector is primarily **random** noise: note that in Figure 3a, the noise contribution to the signal is essentially uncorrelated from one measurement to the next. (There is a technical reason that the noise contributions in Figure 3 in the presence and absence of RDX appear to be different: the reported NQR signal is actually the magnitude of the signal in two orthogonal receiver channels and the noise has a different apparent character, depending on whether the average signal S_b is much larger or much smaller than the standard deviation of the noise, σ_b .)

Figure 3b presents the data of Figure 3a in a histogram display. Again, note the substantial separation between the 'bomb' and 'no bomb' signal intensities. In this set of data, the signal-to-noise ratio is $S_b/\sigma_b = 7.5$, for this sub-kilogram quantity of RDX.

4. Summary

We have shown that pure nuclear quadrupolar resonance (NQR) provides a means for detecting RDX-based explosives in a full-size suitcase geometry.

Advantages of this approach include:

- Sensitivity: Sub-kilogram quantities of RDX-based explosives can be detected in suitcases.
- Specificity: Because the NQR resonance frequencies are highly specific to chemical structure, signals from other nitrogenous materials do not interfere.
- Throughput: An inspection time of 6 seconds is demonstrated in the laboratory.
- No magnets are required, and therefore magnetic media will not be damaged.
- Radiofrequency (RF) field strengths are low, minimizing exposure of RF to operators and allowing the possibility of examining people by NQR.
- An alarm is triggered when the NQR signal from a explosive *anywhere* within the NQR RF coil volume exceeds a preset threshold: operator intervention and interpretation are minimal.
- The apparatus is inherently simple, comprising RF electronics and a computer system.

This NQR approach has been demonstrated for RDX-based explosives in a laboratory setting. Extension to detection of other nitrogenous explosives carried in luggage, mail, small cargo or on a person is anticipated. The technology can be extended to detect certain drugs of abuse. As envisioned, such an NQR explosives detector could be useful in airport and other fixed site installations. The apparatus could be made portable.

5. Acknowledgements

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6. Footnotes and References

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Figure 1

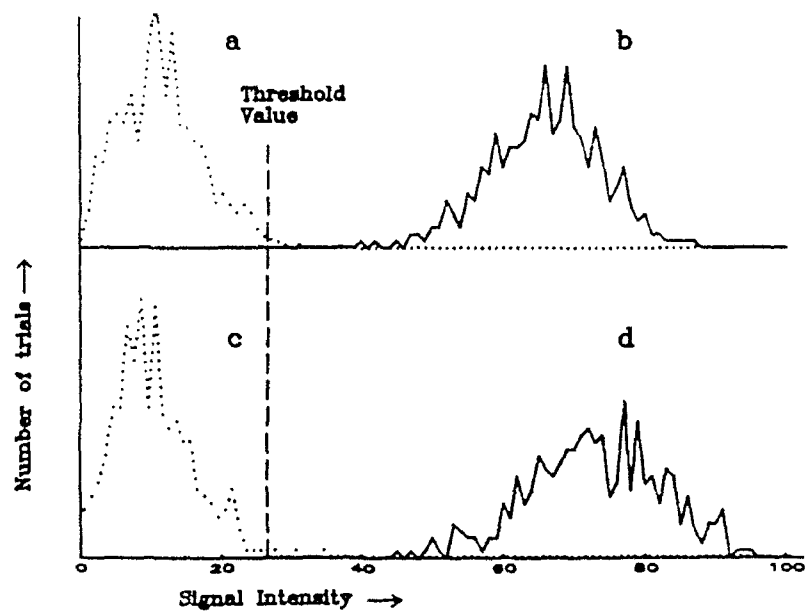
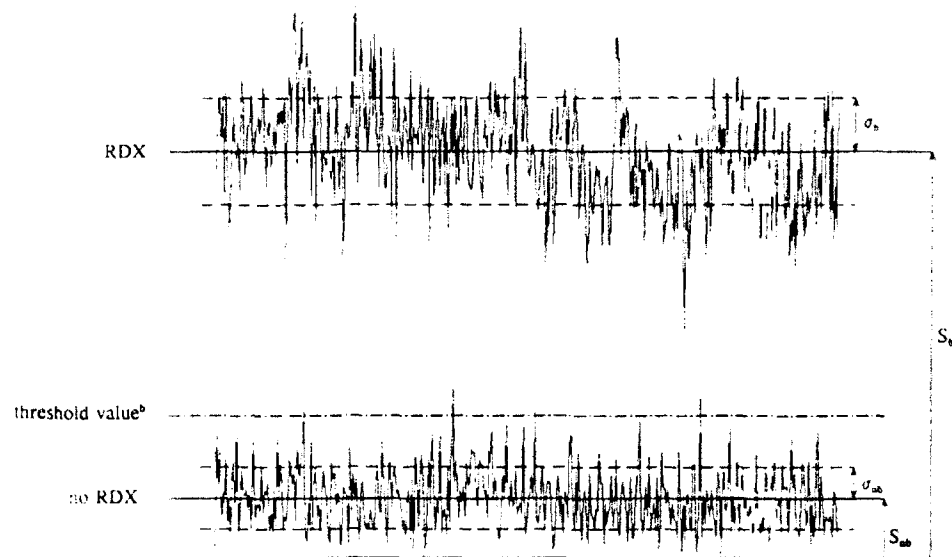


Figure 2

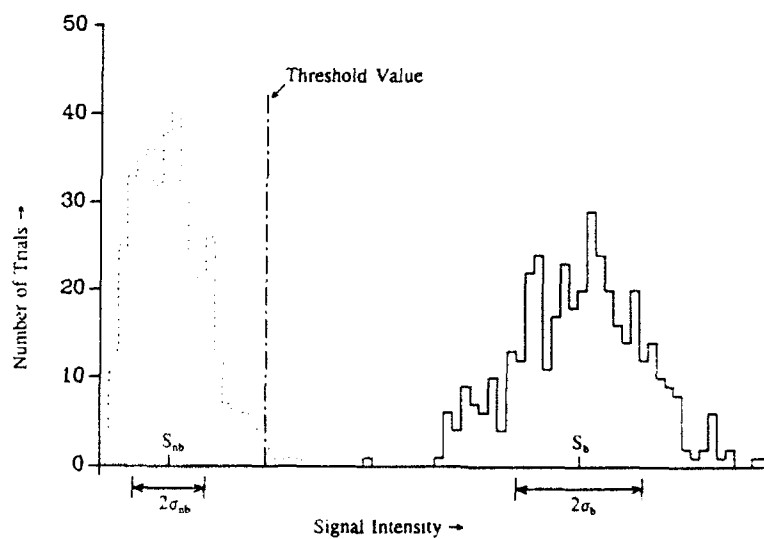
Figure 3a

Naval Research Laboratory NQR Explosives Detector
Detection of RDX*



*Each point represents the result of a single 6 s scan.

*Threshold value set to allow for a 1% false alarm rate.

Figure 3b

HIDDEN EXPLOSIVE DETECTION METHODS

X. LIU, S. FU, H. ZHANG AND J. ZHANG
Explosive Search and Disposal Training Center
Ministry of Public Security
Beijing, China

ABSTRACT. Offenders have been using explosives to commit crimes more and more frequently, employing modern techniques. These explosion and sabotage activities pose a threat to human beings. This paper summarizes hidden explosive detection techniques and methods used in China such as biological technique, explosive vapour detection, technique of marking explosive, X-ray, γ -ray and neutron activation techniques. The advantages and disadvantages of the above methods have been analysed. The development tendency in the field of EOD/IED has also been indicated.

In recent years various activities of explosion and sabotage have become frequent. They do not only pose a threat to every government and their people, but also result in a great economic loss. As a result governments pay more attention to these activities. The aim of explosion and sabotage is not only directed against governmental organizations and senior leaders, but also against civil aviation and railway transportation as well as other nongovernmental organizations. In China in the 1980s, about 1400 bombings took place every year. Since 1990 this number has added up to 3000 every year. Because of a flaw in management regarding explosives in our country, some people often take illegal explosives with them when they go on board of trains or ships. This threatens people's life and public and private property.

In order to control explosives, we have been widely advertising and using different technical measures in some important places, in order to detect illegal explosives. Current detection technology and methods have not been successful in detecting nonmetal "pure explosives". At present, explosive detection technology relates to many subjects including physics, chemistry and biology. On the basis of the detected object (explosive) the detection methods include measuring explosive vapor pressure, nitrogen

elements in explosives and explosive colouration. Technical methods in use are electron capture, ion mobility, gas chromatography, plasma chromatography, mass spectrometry, colouration and bioorganism fluorescence. In spite of the high sensitivity of these methods, the low volatility of many explosives and high quality of their packaging make detection difficult.. False-alarms caused by interference of non-explosive factors confuse inspectors.

We believe that the following methods are feasible:

1. Bio-detection: bio-detection is a method that can provide us with evidence to distinguish between explosives and other materials, by reaction of organisms, when they come in touch with the explosive molecules. For example, we use bacteria and enzymes to detect explosives, because some bacteria and enzymes will change their colour if they come in touch with an explosive. TNT enzyme is used to determine the existence of TNT. This method is very successful, but we have difficulty in using it in practice, because bacteria and enzymes have a short life-time and need strict conditions for their cultivation. We also make use of insects or flies to detect explosives, because they will fluoresce when they come in touch with explosive vapour. With insects or flies the type of explosive can be determined. Field mouse, especially a kind of field mouse growing in Inner Mongolia of China, after breeding and domesticating can be used successfully to detect explosives. Nevertheless some inspectors are not accustomed to detect explosives by using mice and do not like this method. Dogs are world-famous in the field of searching explosives. This method has brought good results. The problem is that the dogs in use are mostly tall and big. When they are searching for explosives in a public place, people often complain about them.

2. Explosive vapour detection: these detection techniques include electron capture, ion mobility, gas chromatography, etc. Most types of explosives have a fixed vapor pressure. Most explosives are electronegative. These explosive compounds when entering the detector, capture some of the electrons to form negative ions, thereby causing a decrease in the detector current. The decrease of negative electrocharge can be indicated by sound, light or by a meter. The vapour detector cannot detect explosives which are hermitically sealed. It also cannot detect explosives whose vapour pressure is very low. The interference of nonexplosive factors may also cause some difficulties.

According to our experience we have developed and produced an explosive detector based on one of the following principles: (a) The explosive detector is portable, light in weight and small in volume, however, the sensitivity is very high and the anti-interference is powerful. (b) The other way is to produce a gateway explosive detector which is combined with X-ray equipment and metal detection gate frame. The detector will not cause any trouble in detection procedure, but raise the detection efficiency.

3. Explosive detection by using multi-energy X-ray: X-ray technology has been used to detect explosives for a long time. Different images will emerge on the screen when X-ray passes through different density materials. Therefore we can determine the materials according to the images on the screen. The detection by using X-ray equipment is efficient in discerning metal products and metal components in explosives. It has difficulty in detecting explosives formed by the elements of carbon, hydrogen, oxygen and nitrogen, especially pure explosives. We have improved X-ray equipment for the past few years. The improved detector makes good use of X-rays, and nonmetal explosives can be detected by using the low energetic part of "soft" X-rays. After this procedure, we can determine the intermediate materials between metal and nonmetal. Different kinds of materials are shown with different artificial colours on the screen. We can clearly determine which is metal, which is nonmetal and which is an intermediate material between metal and nonmetal. These materials can then be classified, and suspected articles can be controlled.

4. To study additives to nitramon and their detection techniques. In many explosive cases in our country criminals use nitramon. It is therefore important to find a good way to detect nitramon. Because the vapour pressure of nitramon is very low, it is difficult to detect it by vapour detection. As most forms of nitramon are powdery, it is difficult to detect it by X-ray. We are studying the way to add some material to nitramon in order to be able to detect it directly and efficiently. We have made good progress. We are required to keep the quality and stability of the explosive unchanged. The material should also not pollute the environment nor give trouble to production technology. The production cost of nitramon should not increase too much. The explosive should be easily detected and the detector should be light, simple to operate and cheap. The technology to add a material to the explosive is closely combined with the research to produce a detector. After the plan is completed, the government will issue an order that explosives without addition must be used up, or destructed, in a limited time.

5. Direct detection of black powder. The technology of black powder is very simple and can be produced in every place. It is frequently used in explosion and sabotage cases in our country. It is impossible to detect black powder directly by vapour detection and much harder to distinguish its shape on screen by X-ray. We have a method to detect black powder by detecting γ -rays produced by K^{40} in black powder. The technical key of this method is to select an appropriate detecting crystal and a suitably designed protection system. To use this technique the following principles should be obeyed: Detecting crystal should work with a high transfer efficiency; its production cost should be low; its useful life should be long; operation should be convenient. The protection system should be designed to be as small and light as possible. Its structure should be simple. It should not be influenced by surrounding effects.

6. Neutron activation analysis. In recent years neutron activation analysis has been adopted to detect explosives. Explosives are detected by radiation of thermal neutrons and fast neutrons. After radiation by thermal neutrons, nitrogen in an explosive can produce γ -rays. Through measuring the γ -rays the existence of an explosive can be determined. But nitrogen can be found in many materials which will release γ -rays by radiation, so the interference produced by these materials often confuses inspectors. Explosives contain not only nitrogen, but also oxygen, carbon, hydrogen etc. Carbon, oxygen and other elements in explosives can be detected by irradiating with fast neutrons. These elements release characteristic powerful γ -rays when irradiated by neutrons. Explosives can be clearly distinguished from other materials according to the different ratios of nitrogen, carbon, oxygen and hydrogen existing in explosives. We combine the X-ray inspection with neutron activation analysis so as to detect explosives quickly, because no direct image can be seen when using only neutron activation analysis.

TESTING PROTOCOL FOR SURFACE-SAMPLING DETECTORS

P. NEUDORFL, M. A. MCCOOEYE and L. ELIAS

Institute for Aerospace Research

National Research Council

Ottawa, Canada

K1A 0R6

ABSTRACT. The use of surface sampling and on-site analysis is a recent innovation in "sniffer" technology designed to counter the bomb threat in civil aviation. Augmenting the previous vapour sampling approach, new detector technology is emerging which allows the rapid detection of nanogram quantities of plastic explosive residue which may be present on the exterior of passenger luggage or air cargo as a result of secreted explosives. In assessing the efficacy of a new detector system, the problem arises of providing a realistic and reliable source of plastic explosive residue with which to challenge the detector. This paper describes several laboratory and field-simulation approaches, and presents results obtained with the most quantitative of these techniques, a "calibrated" thumbprint source.

1. Introduction

For many years the National Research Council of Canada (NRC) has been involved in the testing and evaluation of explosives detectors ('bomb sniffers') for use in civil aviation security. In this area, close collaboration is maintained between NRC, a research institution of the Federal Government, and the Transport Canada. Most of the instruments studied in the past relied on the presence of explosives vapours (EGDN, NG, DNT, etc.) for the detection of hidden explosives, and the methodology for testing of such equipment was described at our previous Symposium in Mannheim [1].

Vapour sniffers, as a rule, will not detect plastic explosives (based on RDX and PETN) unless the material is contaminated with volatile compounds such as EGDN. This is because the vapour pressure of RDX and PETN at room temperature is very low [2] and, in addition, the vapours are strongly adsorbed on most surfaces and thus unavailable for sampling under most field conditions. The inability of traditional bomb sniffers to detect plastic explosives has always been a deficiency, and considerable effort has been directed towards finding a solution to this challenging problem.

Two different approaches have been taken recently to accomplish the detection of plastic explosives by sniffer technology. One approach, promoted by the International Civil Aviation Organization (ICAO), was to mark or tag plastic explosives with small quantities of volatile compounds to make them detectable with existing vapour detectors. The ICAO Convention on the Marking of Plastic Explosives for the Purpose of Detection was signed in Montreal in March 1991, and the production of marked explosives started soon afterwards in some countries.

The other approach was to develop new types of explosives sniffers, capable of detecting unmarked plastic explosives, i.e., RDX and PETN *per se*. These detectors, in general, rely on

traces of solid residue, microparticles, of RDX and PETN, left inadvertently on various surfaces by a person handling plastic explosives (eg., the bomb maker) or by a person who touched a contaminated object (an accomplice). Although the detectors, as a rule, are capable of detecting vapours of RDX or PETN, the probability of collecting sufficient quantities of RDX or PETN vapours is not very high and probably much lower than finding particles of plastic explosives.

Most of the plastic explosives sniffers are composed of two main components: a sampler (or sampling train) and an analyzer. The sampler's function is to remove particles of RDX or PETN from surfaces, by suction, wiping, brushing, or by other means, and gather them on a filter or a special collecting surface; the collector is then heated to vapourize the explosives particles and bring the vapours to the analyzer for detection. The analyzer, which is the heart of the instrument, is based on techniques such as Gas Chromatography (GC), Ion Mobility Spectrometry (IMS), Mass Spectrometry, etc..

With the advent of particle detection technology, the need arose to generate known and controllable microscopic quantities of plastic explosives on different surfaces. Such explosive particle standards are useful not only for a quantitative assessment of the various detectors, but also for the development and optimization of sampling methodology.

In this paper, various methods of explosive particle generation, as tested in the Laboratory, will be discussed. Before discussing particle generation, however, a brief overview of the whole testing protocol for surface sampling detectors will be given.

2. Testing Protocol

Testing of the detectors is carried out in two stages. The first stage consists of *quantitative laboratory evaluation* in which the range of explosives detectable by the device is tested and its sensitivity, or lower detection limit, is assessed. Not all laboratory tests require the generation of explosives particles. For example, sensitivity evaluation of the analyzer itself to various explosives could be adequately carried out with standard solutions of pure compounds deposited on the collecting surface. This simulates particles being captured on that surface. But, when the overall system is evaluated, i.e. the sampler/analyzer combination, the use of particle sources is mandatory. Such tests, if conducted properly, can provide unique information about the efficiency of the sampler as to the removal of the particles from surfaces and their transfer to the analyzer. Such information is needed to optimize the performance of the instrument, particularly the sampling train.

The second stage of the evaluation involves *qualitative operational testing* which is conducted with actual suitcases and real explosives. The purpose of these tests is to get some information about the efficacy of the device as a searching tool. The explosives are concealed in suitcases under conditions which provide varying degrees of difficulty for the detectors used to find them. For example, the first or "easy" level of difficulty involves an explosives handler (the bomb maker) packaging a quantity of plastic explosives in a small box and placing it inside luggage packed with clothing; more difficult cases involve the handler and one or more accomplices. Such practical tests, although very demanding, provide the most realistic assessment of the capabilities of the detector. The tests have to be repeated several times before any conclusions can be drawn. Operational testing with suitcases will not be discussed in this paper.

3. Generation of Explosive Particles

3.1 COATED DUST PARTICLES ON EMERY PAPER

The first attempt to generate particles of RDX and PETN consisted of coating dust particles with standard solutions of RDX and PETN. A fine dust of glass or cellulose was generated by grinding a piece of glass (Pyrex tubing or rod) or cellulose (filter paper) on emery paper. The dust was then coated by depositing solutions of RDX or PETN on the particles and allowing the solvent

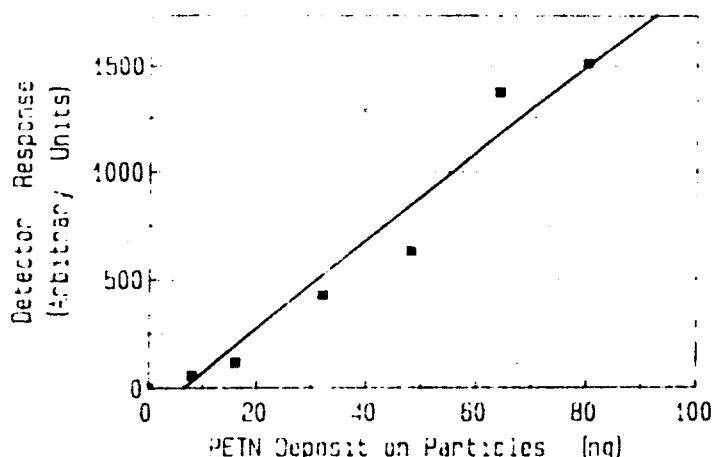


Figure 1. PETN particle source based on coated glass dust on emery paper.

to evaporate. The results of the laboratory testing of such particle sources are shown in Figures 1 and 2. Good correlation was obtained between the amount of PETN and RDX deposited on the particles and the response of the detector (GC/ECD).

To study these sources, a special sampler was used, made of a length of Pyrex glass tubing (6 mm o.d.) fitted with a fine platinum mesh which acted as a filter. The coated particles from the

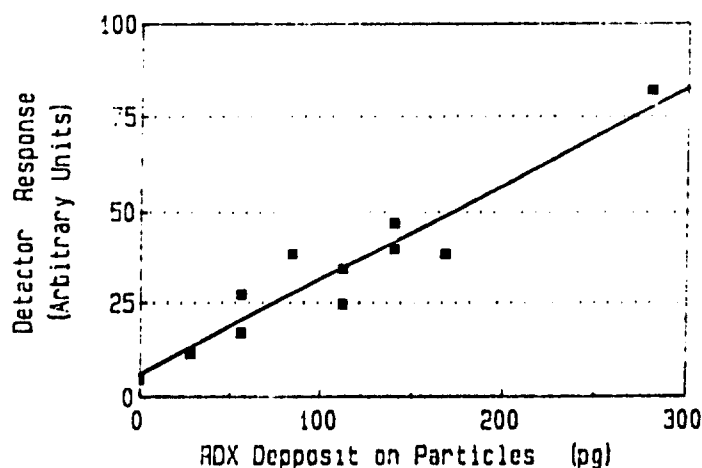


Figure 2. RDX particle source based on spiked cellulose dust on emery paper.

emery paper (Carborundum Diamond Grit 400) were collected on the platinum mesh by means of suction, then heated and thermally desorbed into a laboratory GC/ECD for quantitative analysis. The GC instrument was equipped with a special interface, allowing efficient injection of the vapours from the sampling tubes onto the GC column.

The particle sources based on coated dust have many attractive features, including simplicity, portability, repeatability, and applicability to a wide range of explosives and concentrations. However, such sources suffer from a severe defect: they are not sufficiently realistic in duplicating the actual scenario likely to be encountered in the field. As a consequence, if explosive detectors were designed and optimized on the basis of such unrealistic particle sources, they might be plagued with a high incidence of failure when deployed in the field. For these reasons, it was necessary to search for other, more authentic sources of explosives particles, as described below.

3.2. THUMBPRINTS

When looking for a more realistic source of explosive particles, attention was focused on explosive residues deposited on surfaces in the form of hand or thumbprints. Direct touching of objects with the contaminated hands of an explosives handler, is, after all, the most probable mechanism of transferring explosive traces to various surfaces. If the "explosives thumbprints" could be quantitatively measured and reliably generated on various surfaces, the technique would

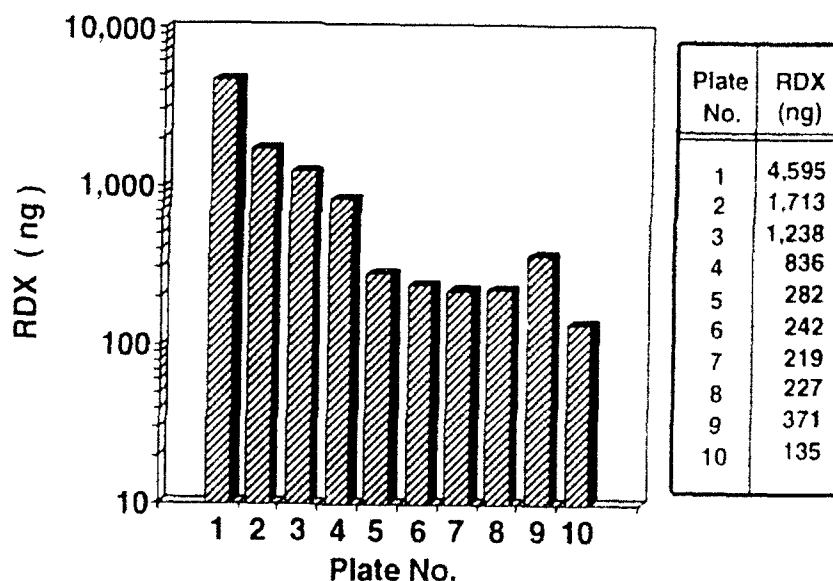


Figure 3. Series of Semtex-H thumbprints on consecutive stainless steel plates: single print per plate. The amount of RDX deposited on each plate is shown.

represent an ideal source of explosive residues for testing and optimization of the detectors.

Before the thumbprints of plastic explosives could be used for such a purpose, however, the methodology had to be developed to analyze explosives residues on various surfaces, and to controllably generate such prints. In the study of explosives thumbprints, we started with stainless steel (SS) plates because they could be easily used and analyzed.

Some results from the study of Semtex-H thumbprints on stainless steel are shown in Figure 3. Ten plates were sequentially touched with a Semtex-contaminated thumb, making a single imprint on each plate. The plates were then rinsed with acetone and an aliquot of the acetone solution

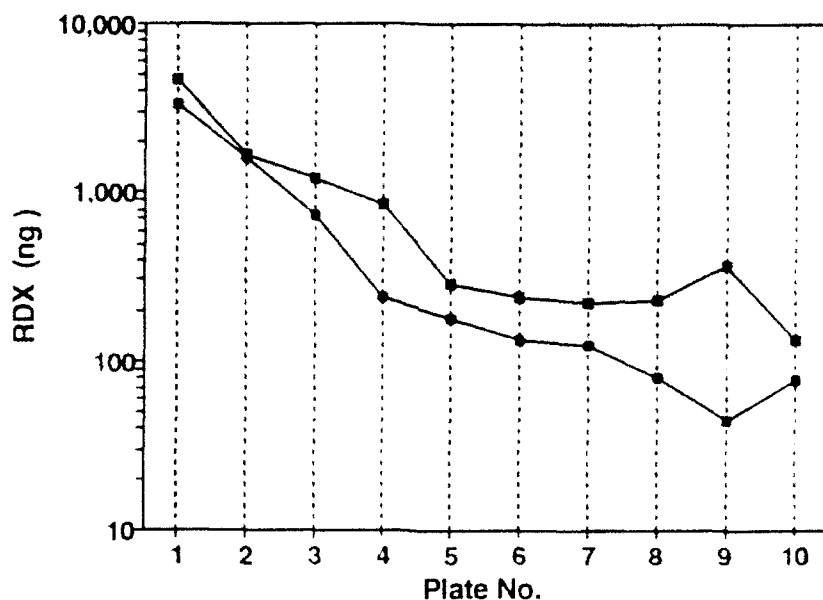


Figure 4. Comparison of two series of Semtex-H thumbprints on stainless steel plates; single print per plate.

analyzed by GC/ECD to determine the quantity of RDX on each plate. Two series of prints were measured and are compared in Figure 4. Each series represents one "inking" of the explosive handler's thumb, i.e., pressing a few grams of the plastic explosive between the thumb and forefinger.

The data in Figures 3 and 4 indicated that the amount of RDX in the thumbprints was in the range of micrograms (10^{-6} to 10^{-7} g), and that after an initial rapid decrease, a certain plateau was reached where the amount of RDX changed only slowly from plate to plate in each sequence. Within the series, one could discern not only a definite trend in the amount of RDX associated with the thumbprints but also find a certain relationship between sequential thumbprints. Thus, if one analyzed only the odd-numbered plates of Figure 4, one could estimate the deposit of RDX on the even-numbered plates reasonably well. The fact that one could estimate the deposit of RDX in the thumbprints without actually analyzing them, represents an important finding, and offers the possibility of having "calibrated" or "standard" thumbprints.

3.2.1. Thumbprint Calibration

Most of the explosive particle sources will be affected and irreversibly changed by the act of sampling, and the source, therefore, must be well defined before being used. Such a condition was automatically fulfilled with the coated dust-on-emery-paper sources, since they were prepared with standard solutions of explosives. The calibration of the explosive thumbprints, however, is a more involved task, requiring a series of thumbprints to be generated in such a way that a correlation between the prints on separate plates can be clearly established. A few selected plates from the series are then analyzed, and the results are used to estimate the deposit of explosive material in the prints on the remaining plates; the latter plates are then utilized as a source of particles for testing of the detectors.

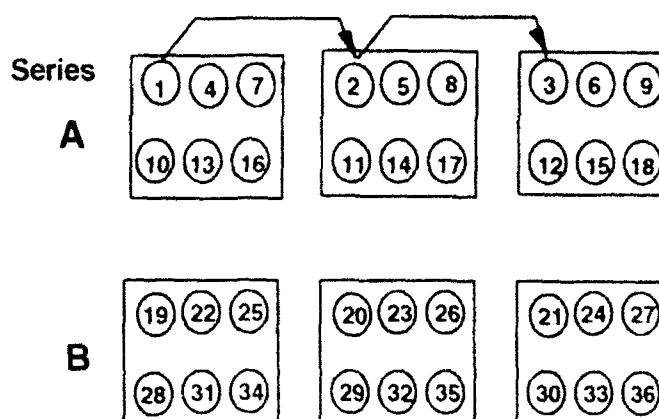


Figure 5. Pattern of generating multiple thumbprints per plate.

3.2.2. Multiple Thumbprints per Plate

Single print-per-plate series tend to generate sources which cover a wide range of values. This is illustrated in Figure 4, where a logarithmic scale was used to plot the data. Although such wide-ranging sources might be required for some applications, more often one needs a large number of nearly identical thumbprints, because many tests have to be repeated several times to become statistically meaningful and, in the optimization studies, only one parameter at a time should be changed.

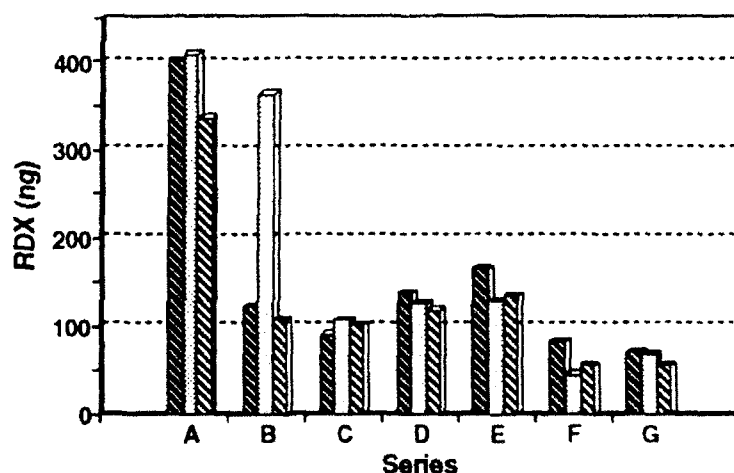


Figure 6. Multiple thumbprints of C-4 on stainless steel plates.

One way to achieve a more uniform distribution of the explosives residues between the plates is to make multiple prints on each plate. Various sequences of touching the plates can be devised

when a large number of thumbprints is involved. Figure 5 illustrates schematically one deposit pattern which was tested: the plates were divided into groups of three, and each group was imprinted as a batch to generate 6 prints per plate. Each batch was made with a fresh "inking" of the thumb. Using such a scheme, seven batches of stainless steel plates (in sets of 3) were stamped, ending with 6 prints of C-4 on each plate. The distribution sequence of RDX imprinted on the plates is shown in Figure 6. Except for one case, Set B, RDX deposits on the plates belonging to the same batch were very similar; by analyzing a single plate in each batch of Figure 6, one could predict the loading on the remaining two plates with about 10% accuracy.

3.2.3. Thumbprints on Various Surfaces

Although most of the thumbprint studies were conducted with stainless steel plates, other materials were also investigated, namely glass, polyethylene, and polyvinylchloride (PVC). Some results from these studies are shown in Figures 7, 8 and 9.

Figure 7 summarizes the RDX results from a series of C-4 thumbprints on glass plates, prepared to check the effect of storage time on the explosive thumbprint. Altogether, 15 glass plates were used in the study, each containing a single thumbprint of C-4. Some plates were analyzed immediately, others were stored between 1 - 6 days before being analyzed. The data showed considerable scatter, but no obvious effect of storage could be discerned for this period of time.

In Figure 8, some data for C-4 prints on polyethylene plates are presented. One side of the

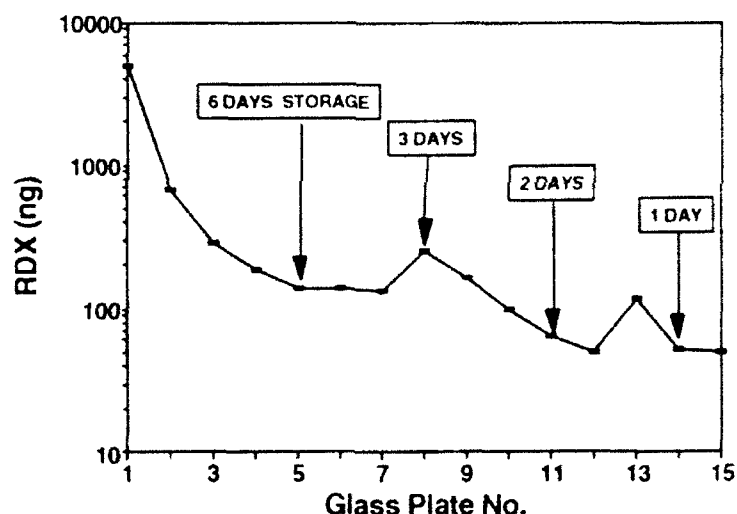


Figure 7. Effect of storage time on thumbprints of C-4 on glass plates; (single print per plate). polyethylene plates was smooth, the other had a matte finish, but both sides provided an excellent surface on which to deposit thumbprints. As Figure 8 illustrates, even with a single print per plate, the RDX data could be plotted on a linear scale and would show a relatively slow, gradual decrease. Since polyethylene could also be washed with acetone, the analysis of explosives residues on polyethylene was straightforward.

Another surface investigated was PVC, a common material for making suitcases. The analysis of explosives residues on PVC, however, required a different approach because direct washing of the PVC surface with acetone created serious contamination problems in subsequent GC/ECD analyses, as acetone partly dissolved the PVC material.

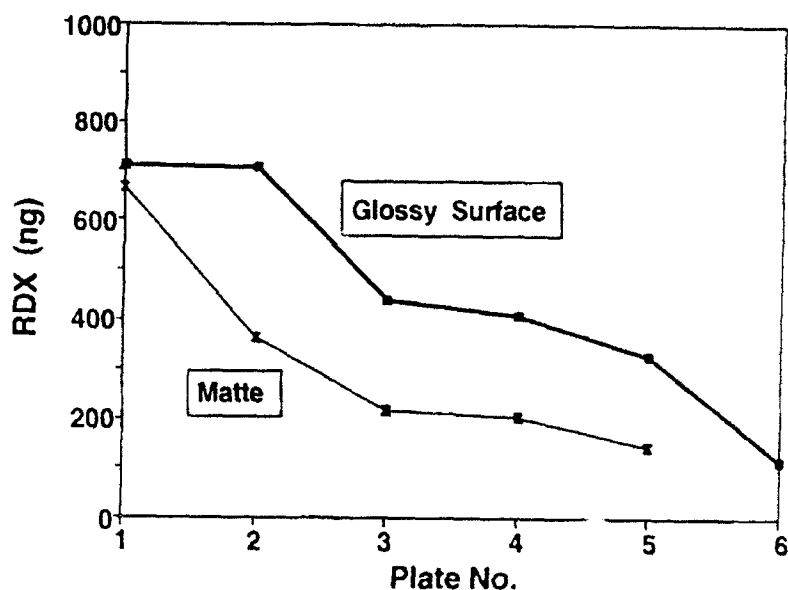


Figure 8. Prints of C-4 on Polyethylene; single print by two fingers (index and middle finger).

Two techniques were found acceptable for analyzing explosives thumbprints on PVC. One relied on wiping the surfaces with a cotton swab dampened with methanol and then extracting the swab with acetone. The other technique, which was slightly less efficient in removing the explosives residues but gave much cleaner background on the GC/ECD, utilized Micropore tape (product of

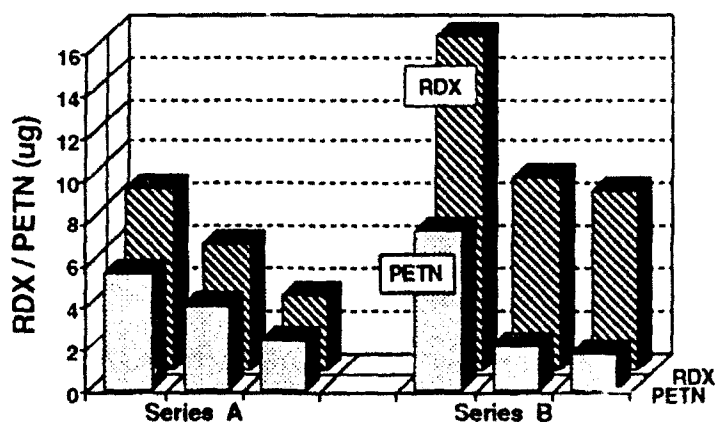


Figure 9. Semtex-H thumbprints on PVC; two series, 4 prints on each plate.

3M) to wipe the PVC surfaces clean without using any solvent. The tape was then extracted with acetone, followed by GC/ECD analysis as before. Control tests indicated that over 90% of explosives residues could be removed by dry wiping with the Micropore tape, as compared to the wet swabbing method.

Some results of the study of Semtex-H thumbprints on PVC are shown in Figure 9. The study utilized three PVC plates, and the experiment was repeated twice (Series A and B). In each experimental series, four thumbprints of Semtex-H were deposited on each plate, according to the pattern of Figure 5. The series A and B were made separately from each other, including a separate "inking" of the thumb before printing of the plates. Both RDX and PETN were determined in the Semtex-H thumbprints on PVC, as shown in Figure 9. The reason for large differences in the ratio of RDX/PETN for Series A and B is not clear.

3.2.4. Thumbprint Analysis and Generation

Since many aspects of the analysis and generation of plastic explosives thumbprints were already covered in the previous sections, the purpose of this section is to provide some information about the instrumentation used in the study, and to comment on certain factors affecting reproducibility of the thumbprints.

For thumbprint quantification, the explosive residues from the surfaces were first transferred into acetone solution, either by rinsing the surface directly or by swabbing the surface and extracting the swab with the solvent, and then the acetone solution was analyzed by GC/ECD. We used a HP 5890 GC equipped with Model 7663 Autoinjector and Model 3396 Series II Integrator. The GC operating conditions are summarized in Table 1.

TABLE 1. The GC / ECD Operating Conditions

Column	DB-5 (10 m x 0.53 mm ID, 1.5 μ film) isothermal operation @ 155°C
Carrier	N ₂ , 30 cm ³ /min
Injector	185°C
Detector	ECD @ 225°C; (N ₂ make-up, 8 cm ³ /min)

Retention times were: PETN 2.0 min, RDX 2.7 min. A typical chromatogram is shown in Figure 10.

The main problem with the thumbprints is their reproducibility. To calibrate a single thumbprint normally requires two other thumbprints to be analyzed, usually its immediate 'neighbours' in the series. This could be a laborious and time consuming task, particularly if a large number of standard thumbprints is needed, as often is the case. If the thumbprints could be generated more predictably and reproducibly, however, less analytical work would be required to characterize them.

The following factors were found to affect the amount of RDX and PETN transferred by thumbprints:

- cleanliness of fingers and plates
- state of explosive surface (i.e., old or freshly exposed)
- explosive type (Semtex, C-4, sheet explosive)
- type of plates (stainless steel, polyethylene, PVC)
- size of finger or thumb
- pressure applied to imprint
- personal variations (skin texture, roughness, etc.).

The generation of reproducible thumbprints is more akin to an art than a science, and as such, requires some skill and practice. Among the most important factors, relatively easy to control.

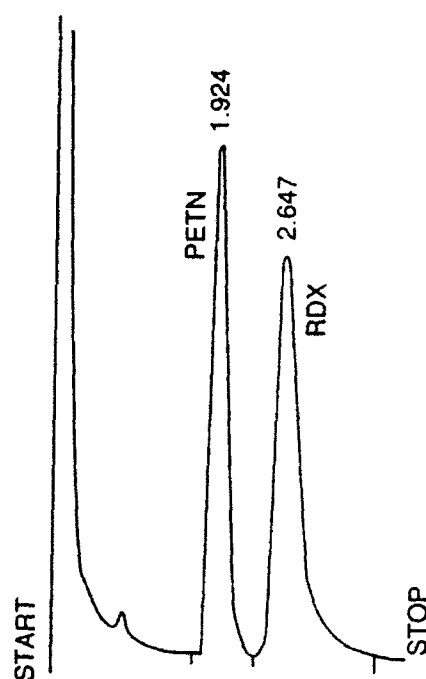


Figure 10. Chromatogram of Semtex-H residues recovered from a stainless steel plate. 1 μ L of acetone aliquot was injected, containing 370 pg PETN and 265 pg RDX.

is cleanliness of the fingers and the plates used for making the prints. Any dust and grease on the plates or hands could prevent good contact and affect the strength and reproducibility of the thumbprints. Also, if possible, a freshly exposed surface of the explosive should be used for "inking" the fingers. Attempts to control the pressure on the finger by placing a certain weight on it while touching the surface, or masking the thumb to control the size of print, were made, but produced no better results than those obtained "freehand".

4. Testing of Detectors with Thumbprints

To illustrate the kind of information that can be obtained in evaluating surface-sampling detectors using the thumbprint method described above, some actual test results are presented in Tables 2 and 3.

The data in Table 2 refer to a commercial prototype explosives detector which utilizes a powerful vacuum cleaner to remove explosive residues from surfaces. The sampling nozzle, at the end of a vacuum hose, resembled a suction cup, allowing very close contact with the surface. The particles were collected on a filter located some distance from the sampling nozzle, then heated, vapourized and transferred to the analyzer, which is integrated with the sampling train of the detector. The analyzer was tested separately with standard solutions of RDX, and its lower detection limit was less than 1 ng RDX (10^{-9} g).

The detector was then tested as a whole with the thumbprints of Semtex-H on stainless steel plates. Three sequentially stamped plates were used, Nos. 1 and 3 for challenging the detector, and the middle plate, No. 2, as a reference. Both testing plates generated an RDX alarm: the signal from No. 1 was well above the alarm threshold, whereas that from No. 3 was very close to the threshold.

Table 2. Testing of a Surface-Sampling Detector with Semtex-H Thumbprints on Stainless Steel Plates

Plate No.	1	2	3
Touched by Semtex-H Contaminated Thumb	Yes	Yes	Yes
Sampled by Explosive Detector	Yes	No	Yes
Signal Generated	5930	None	3950
Alarm Threshold of 3500	Alarm!		Alarm
RDX Quantity <u>Remaining</u> on the Plate	<u>1.22 μg</u>	1.20 μg	<u>1.09 μg</u>

Perhaps the most revealing results in Table 2 were the amounts of RDX found on plates 1 and 3, *after being sampled* by the detector. In comparison with plate No. 2, the one *not* sampled, it would appear that the sampling process was so inefficient in removing the explosive residues

Table 3. Testing of a Surface-Sampling Detector with Thumbprints of Explosives Deposited on Stainless Steel Plates.

Explosives	Alarm Generated		Analysis of the Plate	
	PETN	RDX	PETN, μg	RDX, μg
US Sheet (PETN)	Strong	None	11.9	0.0
C-4 (RDX)	None	Strong	0.0	0.10
Semtex-H (RDX, PETN)	Weak None	Strong Weak	33.8 6.2 *	5.88 0.83*

*) Plate analyzed after being sampled with the detector.

from the surfaces that it made essentially no difference in the analyses whether the plates were sampled or not. Also, if the amount of RDX on the plates, about 1 μg RDX, is compared with the lower detection limit of the analyzer of 1 ng, it was evident that the weak point in the performance of the detector was not caused by the analyzer but by the sampling component. Thus, major improvements in the detection capability of the instrument could be obtained if the efficiency of sampling were improved. A particular issue to address is how to remove explosives residues efficiently from the surfaces. The data in Table 3 were obtained from tests of another explosive particle detector. The detector's sampling system also relied on suction; however, the sampling nozzle was fitted with a brush, and the released particles travelled only a short distance before being trapped on a collection surface. The analyzer of this device could detect several

nanograms of PETN, and less than 1 ng RDX. The data of Table 3 indicated that considerable differences may exist in detectability of various explosives deposited on the same substrate and that the residues of Semtex-H, in particular, were rather difficult to detect. The quantitative data for PETN and RDX in Table 3 refer to reference plates not sampled by the detector (except of the second entry for Semtex-H, as indicated). When comparing the performance of the detector as a whole with the capabilities of the analyzer itself, one must conclude, again, that the sampler's efficiency was poor, with respect to the removal of particles from surfaces.

5. Conclusions

The introduction of surface-sampling detectors as technical aids in law enforcement represents a qualitative change in the strategy on the detection of plastic explosives. Whereas, in the past, the emphasis was on vapour preconcentration and maximum sensitivity of the analysis, now the most critical component has become sampling effectiveness. This conclusion is predicated on the fact that a single particle of explosives carries enough quantity of the material, nanograms or more, to be easily detectable by most existing analyzers. The problem, then, is to ensure that such particles would indeed be detected if they were present on the surface, which means that one needs an effective search strategy and well-designed sampling system.

To test and optimize such sampling systems requires realistic sources of explosives particles. Our approach, though somewhat labour intensive, provides such sources through the use of actual handprints of real explosives on various surfaces.

The utility of our particle sources is illustrated in the results obtained from the testing of two prototype surface-sampling detection systems. The results of these tests delineate a marked weakness in the sampling train of these system

6. Acknowledgements

The authors acknowledge with thanks the contributions of D. E. Wilson of Transport Canada, and E.B. Stimson and G. Scaiano of this laboratory.

7. References

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EXPLOSIVE AND TAGGANT DETECTION WITH IONSCAN

LUCY L. DANYLEWYCH-MAY & CAMERON CUMMING

Barringer Research Limited

304 Carlingview Drive

Rexdale, ON, Canada, M9W 5G2

ABSTRACT. A study of a number of commercial explosives and proposed taggants was performed with a commercially available Ion Mobility Spectrometer (IMS), IONSCAN, manufactured by Barringer for detection of explosives and drugs. The ion-molecule chemistry, i.e. the type of ions formed in the ionization chamber, and the stability of the formed ions when subjected to the IMS detector environment are affected by several IMS operating conditions. The operating temperature and the reactant ion are the two dominant factors in dictating which particular ions are detected from a molecular species introduced in a vapor (or gaseous) form into the reaction region. For a low false alarm it is desirable to select operating conditions in such a way that multiple ions are formed from the same molecular species. Ion identification under different operating temperatures and reactant ions for many explosives of interest and taggants proposed by ICAO are reported in this paper. Results of laboratory and field tests of false alarm rate (FAR) are reported for both discrete and continuous modes of operation of IONSCAN. Different sampling techniques for volatiles such as the International Civil Aviation Organization (ICAO) taggants and non-volatile explosives or explosives-related substances are discussed. Advantages and/or disadvantages are evaluated for each type of sampling technique.

GLOSSARY OF ABBREVIATIONS, ACRONYMS AND SYMBOLS

BRL	Barringer Research Limited
DMDNB	2,3-Dimethyl-2,3-dinitrobutane
DNT	Dinitrotoluene
EGDN	Ethylene glycol dinitrate
EVD	Explosives Vapour Detector
FAR	False Alarm Rate
FWHM	Full Width at Half Maximum (of an IMS peak)
HMX	Cyclo-1,3,5,7-tetramethylene-2,4,6,8-tetranitramine
ICAO	International Civil Aviation Organization
IMS	Ion Mobility Spectrometer
ISM	IONSCAN System Management (software)
K_0	Characteristic Reduced Mobility of Ions
LCD	Liquid Crystal Display
MW	Molecular Weight
NG	Nitroglycerine
OMNT	ortho-Mononitrofluene
P_d	Probability of Detection
PC	Personal Computer
PCDA	Personal Computer Data Acquisition
PETI	Pentaerythritol Tetranitrate
PMNT	para-Mononitrofluene

RDX	Cyclo-1,3,5-trimethylene-2,4,6-trinitramine
Semtex-A	Czechoslovakian plastic explosive containing PETN
Semtex-H	Czechoslovakian plastic explosive containing RDX and PETN
TDC	Transportation Development Centre
Tetryl	Trinitro-2,4,6-phenylmethylnitramine
TNT	Trinitrotoluene

1. Introduction

1.1 BACKGROUND

The ever-increasing threat of the illegal use of explosives in public areas, and more specifically in airports and aircraft, has resulted in an urgent need for screening devices capable of explosives detection. Current technologies are inadequate for rapid and efficient security screening of either the passengers or their luggage. The time needed for sampling and analysis is excessive and disrupts the passenger flow in airports. More sensitivity and speed is required to achieve the desired levels of security and to minimize passenger disruption. An Ion Mobility Spectrometer (IMS), offers interesting features for passenger and luggage inspection at airports.

1.2 APPROACH

The science of ion mobility spectrometry, also called plasma chromatography, is over twenty years old; the early work was reviewed by Karasek (1976). The fundamentals of IMS have been published in a monograph Carr (1984). This paper reports on the detection of explosives and ICAO-approved taggants with the unique IMS known as the Barringer IONSCAN, and on continuous in-line sampling and analysis of airline baggage.

The overall sensitivity and reliability of IMS detection was improved by optimizing ionization conditions, ionization chamber dimensions, temperatures, and flows. IMS data were obtained on a wide variety of internationally available explosives, including commercial explosives (the components of which can effect the ionization mechanisms), and ICAO taggants. Software improvements were implemented for continuous on-line sampling operations, for enhanced sensitivity and lower false alarm rate (FAR) in explosives detection.

The use of cyclones and vacuum impactors for particulate preconcentration has not proved to be particularly satisfactory, often causing contamination and clogging which cannot be tolerated in the envisaged high throughput airport conditions. Means of improving or eliminating these devices were investigated, particularly the use of a reel-to-reel tape and direct flow-through collection. The impact of alternative approaches on the collection tape, and the cost and performance of alternative tape substrate materials were also investigated.

2. Ionscan Detector Optimization

Using ^{63}Ni as an ionization source and air as drift and carrier gas the free electrons are converted to primarily $(\text{H}_2\text{O})^+\text{m.O}_2^+$ ions. The ion chemistry in the IONSCAN can easily be modified by changing reactant ion through introduction of a suitable dopant to facilitate formation of molecular

ions and molecule-ion clusters from trace compounds. The types of ions formed from several explosive substances and taggants of interest are discussed here.

A commercially available instrument from Barringer Inc., shown in Figure 1, is based on an ion mobility spectrometer (IMS) as a detector. The major differences between the IONSCAN and other commercially available units are the flexibility in temperature controls in three regions: sample desorption, sample transfer line which is connected to the reaction chamber, and the drift tube. IONSCAN also has flexibility in selection of electric field, polarity, electronic gate pulse width and frequency and sample desorption duration.

The selection of reactant ion also can be easily changed. An independent temperature control of the desorber and ease with which either liquid, solid or preconcentrated vapour samples can be introduced into the IMS ionization chamber allows great flexibility in studying different compounds of interest.

The basic IONSCAN detection system is shown in Figure 1.

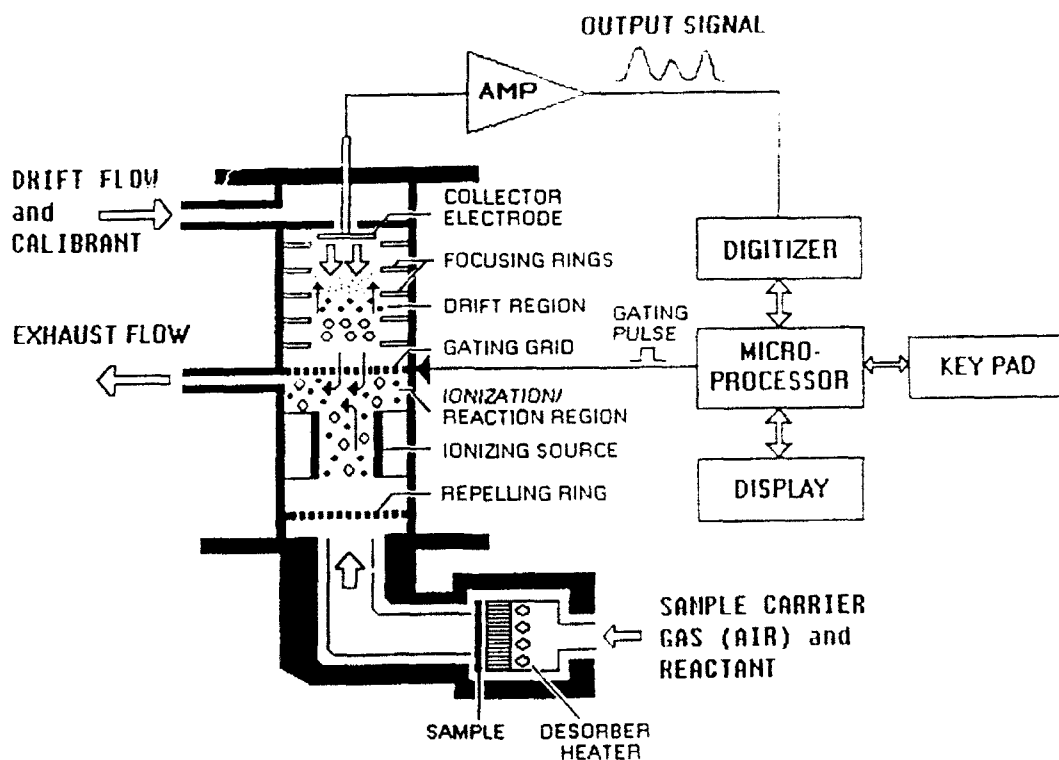


Figure 1. Basic IONSCAN Detection System

The sample is vaporized in the desorber and is carried through the transfer line to the ionization/reaction chamber in a flow of dry air carrier gas containing a chlorinated reactant. The vapours are ionized by a ^{63}Ni beta-ray source. Explosives and taggants form negative ions which are gated at intervals of 24 ms into the drift tube, through which they move to a collector electrode under the influence of an electric field and against a counterflow of dry air drift gas containing a small amount of calibrant. The drift times required to reach the collector electrode

are inversely proportional to the characteristic reduced mobilities (K_0) of the ions, and the ratio of their drift times to the drift time of the internal calibrant is the means of identifying the explosives and taggants present in the sample. The collector electrode current is amplified and digitized electronically, and analyte signals are enhanced and validated by microprocessor algorithms.

Detector optimization involved investigating the effects of:

- ionization/reaction chamber dimensions on ionization enhancement (Section 2.1);
- drift tube temperature on ion stability and detection limits (Sections 2.2 and 2.3);
- commercial explosive composition on ion peak intensities (Section 2.3).

2.1 IONIZATION/REACTION CHAMBER

Earlier experiments with IONSCAN were carried out at high temperatures in all three domains. Some explosive molecules were detected as simple molecular ions (eg DNT, TNT, RDX), and others as the decomposition product NO_3^- (eg EGDN, NG, PETN). This method of detection was non-specific for several explosives and prone to high FAR due to single peak detection for all of them. To improve specificity and reduce FAR, the temperatures of the three domains were independently optimized. At the new lower temperatures with a carefully selected reactant dopant ion, multiple peak detection from a single molecular explosive species became possible. This reduced greatly the FAR, with some loss of sensitivity (since the species was now distributed amongst more than one ion). Further optimization of the reaction region restored the original sensitivity for most of the explosives and taggants, and enhanced the sensitivity for others.

2.2 DETECTION OF ICAO TAGGANTS

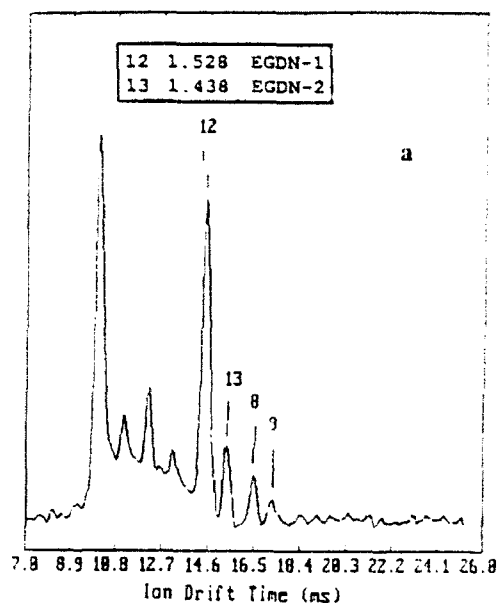
ICAO have mandated that volatile taggants be added to involatile plastic explosives during their manufacture to aid in the detection of plastic explosives. The manufacturer will select a taggant from those specified by ICAO -- EGDN, OMNT, PMNT and DMDNB. For example, EGDN is now added to Semtex-H.

Earlier studies showed poor IONSCAN sensitivity for these taggants, due to lower ionization efficiency in the ionization/reaction chamber, and due to ion and ion/molecule cluster instability in the drift tube at its elevated temperature. The taggants were therefore reevaluated using the longer ionization/reaction chamber (as described in 2.1 above) to improve ionization efficiency, and lower drift tube temperatures to reduce ion breakdown.

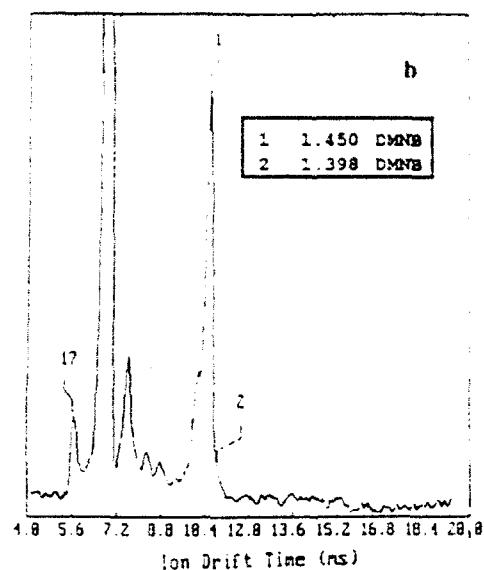
Plasmagrams are shown in Figure 2. The inferred chemical identity of the ion formed from different explosives or explosive taggants was based partially on previously identified ions in the literature using IMS/MS and by enhancing peak intensity by changing the reactant ion in the ionization chamber. In addition to the above a plot of drift time as a function of ion mass shown in Figure 3 was used to infer mass of other ions that could not be identified otherwise. The drift times at different temperatures were normalized to the drift time of $(\text{TNT-H})^+$ at 100°C . Reduced mobilities were also calculated based on measured drift times and assumed reduced mobility for $(\text{TNT-H})^+$ to be $1.450 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. This value of reduced mobility was arrived at from calculations at high temperature (260°C) and assuming $(K_0)\text{NO}_3^- = 2.44$ and $(K_0)\text{Cl}^- = 2.74 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

At an operating temperature of 100°C the two proposed explosive taggants, EGDN and DMDNB, could not be detected. By lowering the IMS operating temperature to 50°C the two taggants were easily detected. All other explosives previously mentioned showed the same basic ion pattern

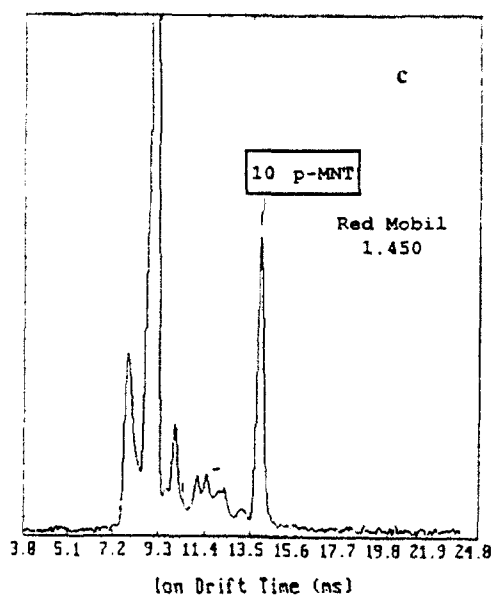
ETHYLENE GLYCOL DINITRATE (EGDN)



DIMETHYLDINITROBUTANE (DMNB)



Para-MONONITROTOLUENE (p-MNT)



Ortho-MONONITROTOLUENE (o-MNT)

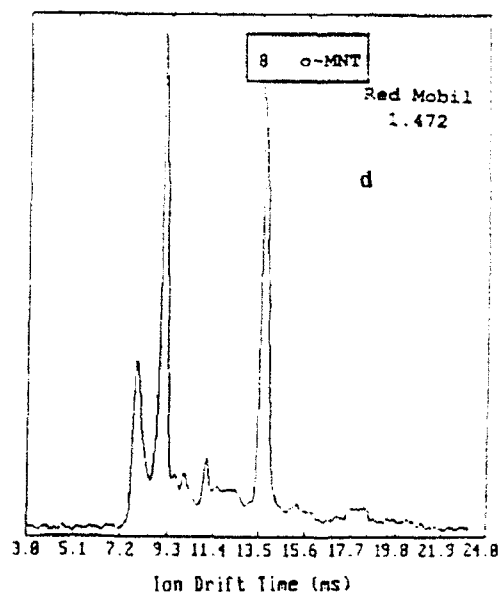


Figure 2. IONSCAN Plasmagrams of taggants

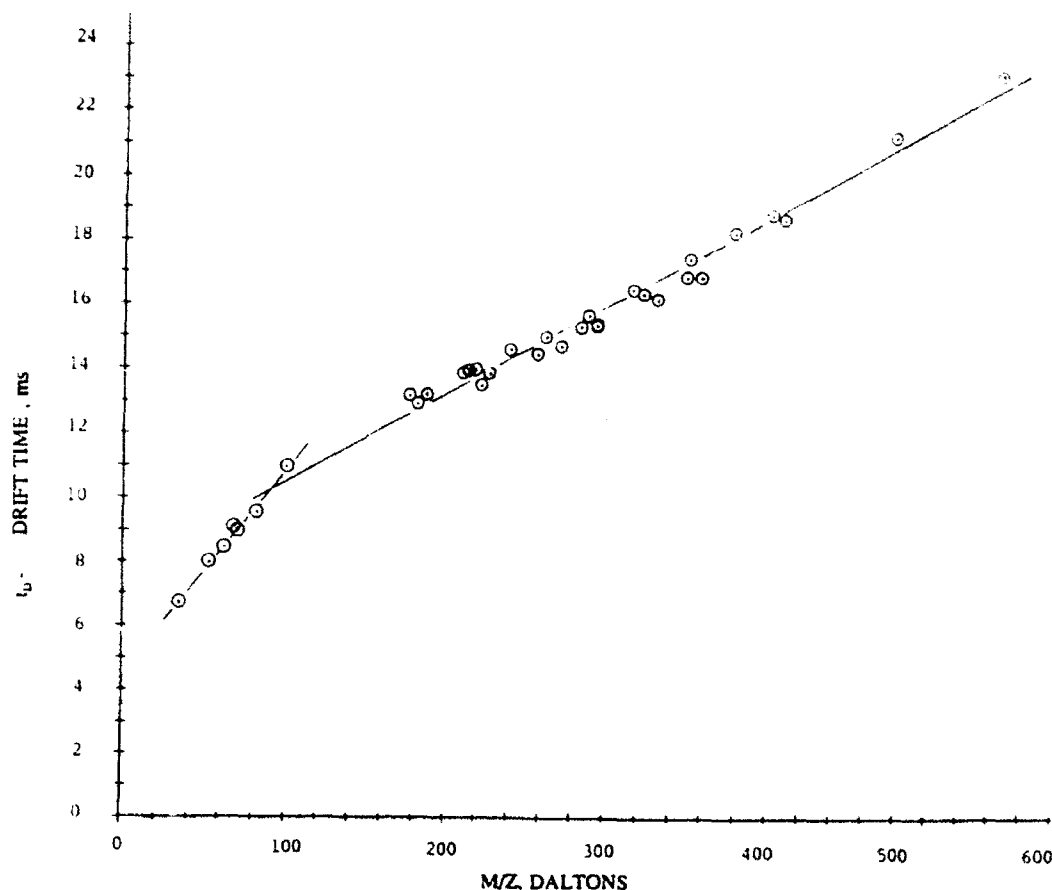


Figure 3. Plot of Drift Time versus Reduced Mass for Explosives Ions

The two peaks observed for EGDN are associated with chloride and nitrate ion attachment to the EGDN molecule. The intensity of the nitrate peak is about one third of that of EGDN.Cl⁻ ion when pure EGDN is used. The EGDN plasmagram is shown in Figure 2a. Traces of NG (peaks 8 and 9) are observed in this record.

Increasing traces of the NO₃⁻ ion concentration in the reaction chamber enhances EGDN.NO₃⁻ formation; however replacing Cl⁻ reactant ion with NO₃⁻ ion resulted in almost complete disappearance of both EGDN ions. Similar results were obtained with NG at 100°C and 50°C IMS operating temperatures.

The ions observed from DMDNB (Figure 2b) are proton abstracted ions, and chloride and nitrate ion attachment. The effect of the NO₃⁻ ion concentration in the reaction chamber was similar to that of EGDN and NG.

The taggants PMNT (Figure 2c) and OMNT (Figure 2d) are detected readily by chloride ion attachment in the long reaction chamber at 50°C.

IONSCAN reduced mobility data for the ICAO taggants are summarized Table 1.

Table 1
IONSCAN Reduced Mobility Data for Taggants

<u>Taggant</u>	<u>MW</u>	<u>(M-H)⁺</u>	<u>M.Cl⁻</u>	<u>M.NO₃⁻</u>
EGDN	152		1.528M	1.438m
DMDNB	176	1.556m	1.450M	1.388m
OMNT	137		1.472M	
PMNT	137		1.450M	

* m = minor, M = major

The separate effects of chamber length and drift tube temperature on detection limits of taggants are shown in Table 2.

Table 2
Effect of Ionization/Reaction Chamber Length and Drift Tube Temperature on Taggant Detection Limits

<u>Drift Tube Temperature</u>	<u>Chamber Dimensions</u>	<u>Detection Limits (ng)</u>			
		<u>OMNT</u>	<u>PMNT</u>	<u>DMDNB</u>	<u>EGDN</u>
100°C	Standard	25	25	nd	nd
100°C	Long	25	25	25	nd
50°C	Standard			5	5
50°C	Long	1	1	0.5	0.1

Table 2 shows significant sensitivity improvements for EGDN and DMDNB, both at lower temperatures and in the longer ionization/reaction chamber. OMNT and PMNT sensitivity did not improve in the longer chamber at 100°C, but significant improvement in sensitivity at 50°C was achieved. In general, Table 2 shows that taggants can be detected at levels comparable to those for explosives.

2.3 DETECTION OF PURE AND COMMERCIAL EXPLOSIVES

Previous IONSCAN explosives detection development focussed on pure explosives, and only a limited number of commercial explosives were examined. The IONSCAN explosives data base has since been expanded considerably, with particular emphasis on the acquisition of commercial explosives data. Samples were usually analysed as solids or solutions. Some of the more volatile materials were analyzed as headspace vapours.

IONSCAN IMS data on pure explosives components are given in Table 3. Ion identification is partially based on published data for TNT and DNT and reduced mobilities of Cl^- and NO_3^- (Asselin, 1978, Wernlund, 1978, Spangler, 1978).

Some of the commercial explosives examined are listed in Table 4. Table 4 also shows the explosive components detected by IONSCAN in these commercial materials. IONSCAN plasmagrams for DNT, TNT and NG are shown in Figure 4 and for RDX, PETN, HMX and Tetryl in Figure 5. The various Spanish explosives listed in Table 4 were obtained by Spanish authorities from improvised explosive devices and contain a diverse range and varying number of explosive components.

Table 3

IONSCAN IMS Data for Explosives
 K_0 Values Relative Intensities*

<u>Explosives</u>	<u>MW</u>	<u>(M-H)⁺</u>	<u>M.Cl⁻</u>	<u>M.NO₃⁻</u>	<u>Other Ions**</u>
DNT	182	1.569M	1.438t		
TNT	227	1.450M			1.070hc
NG	227	1.450m	1.345M	1.283m	
PETN	316	1.222m	1.153M	1.104mM	1.063m
RDX	222	1.490t	1.390M	1.315mM	0.950hc
HMX	296	1.316t	1.248M	1.194mM	
Tetryl	287		1.213M	1.193mM	1.385t 0.871hc

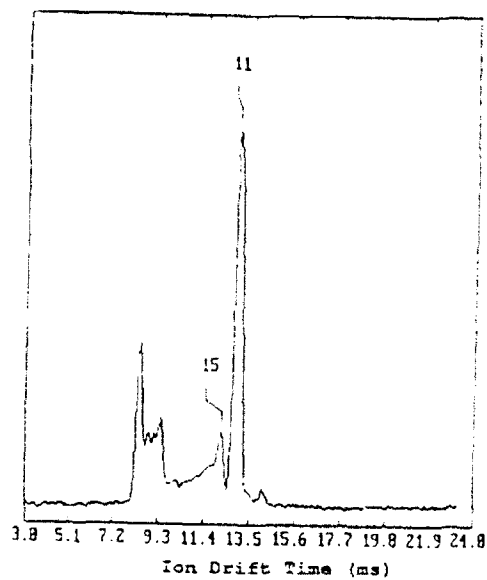
* Intensities in pure and commercial explosives, excluding those containing ammonium nitrate, which cause characteristic changes in intensity patterns.

m = minor; M = major; mM = variable; t = trace;

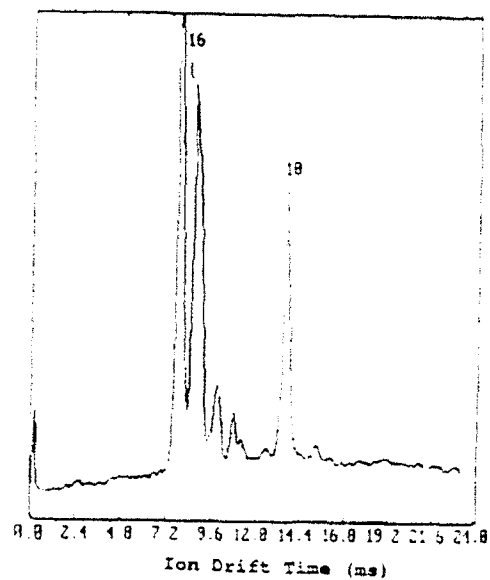
hc = at high concentration

** TNT M.(M-NO₂)⁺; PETN M.ClO₃⁺; RDX M.(M.Cl)⁺;
Tetryl (M-NO₂)⁺ and M.(M.-NO₂)⁺

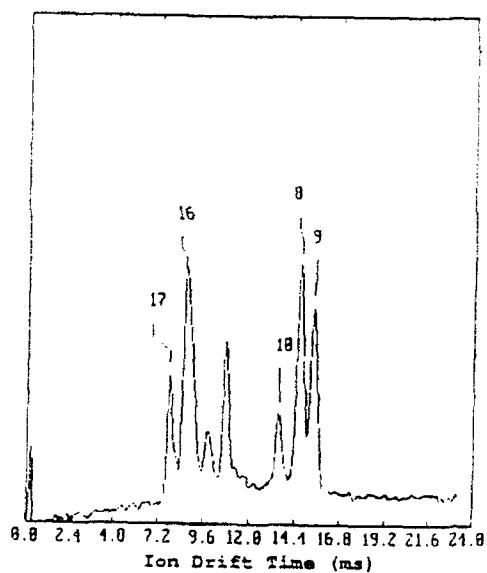
DNT Solid



TNT Solid



NG Vapour



Peak No	Ret Mobil	Peak Identity
8	1.340	NG-1
9	1.276	NG-2
10	1.451	NG-3/TNT
11	1.566	DNT
15	1.652	Calibrant
16	2.295	Reactant
17	2.537	Cl ⁻

Figure 4. IONSCAN Plasmagrams of DNT, TNT and NG Explosives

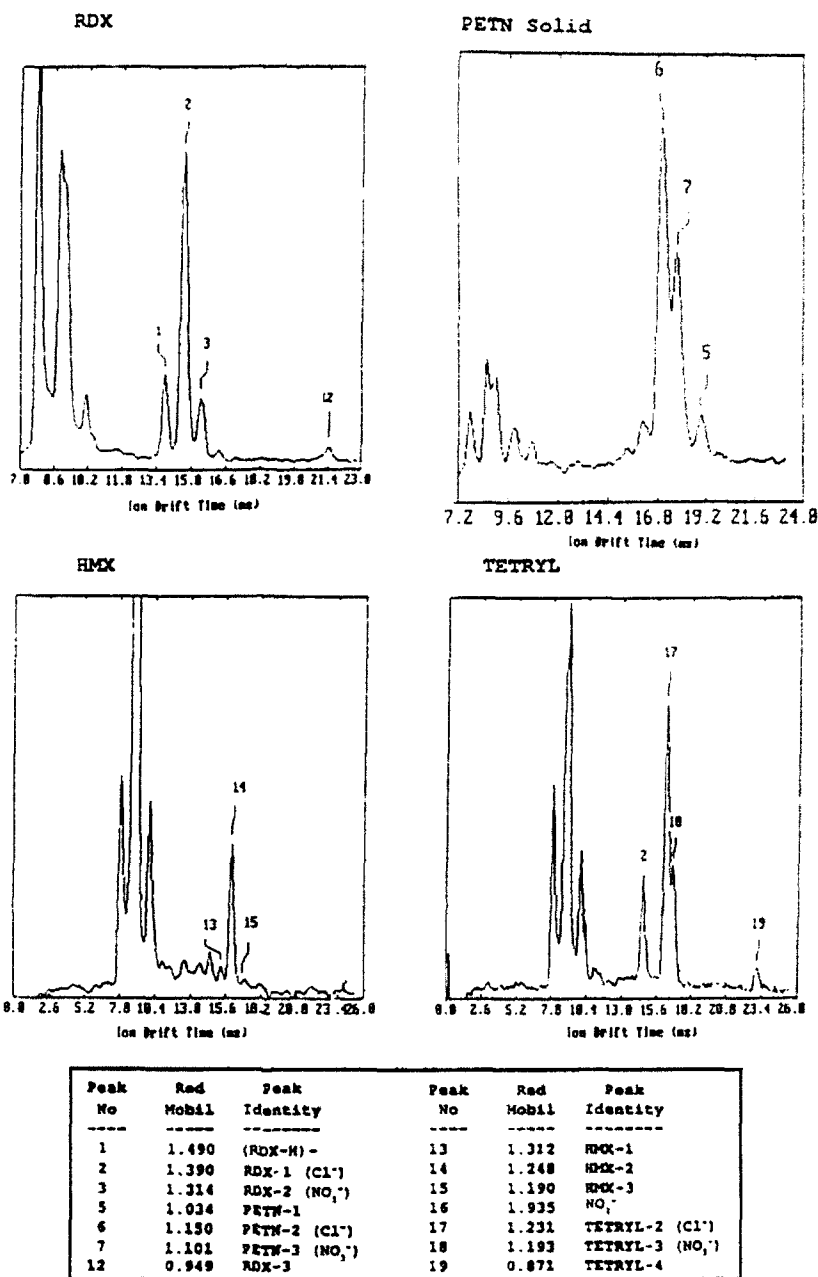


Figure 5. IONSCAN Plasmagrams of Pure RDX,PETN, HMX and Tetryl Explosives

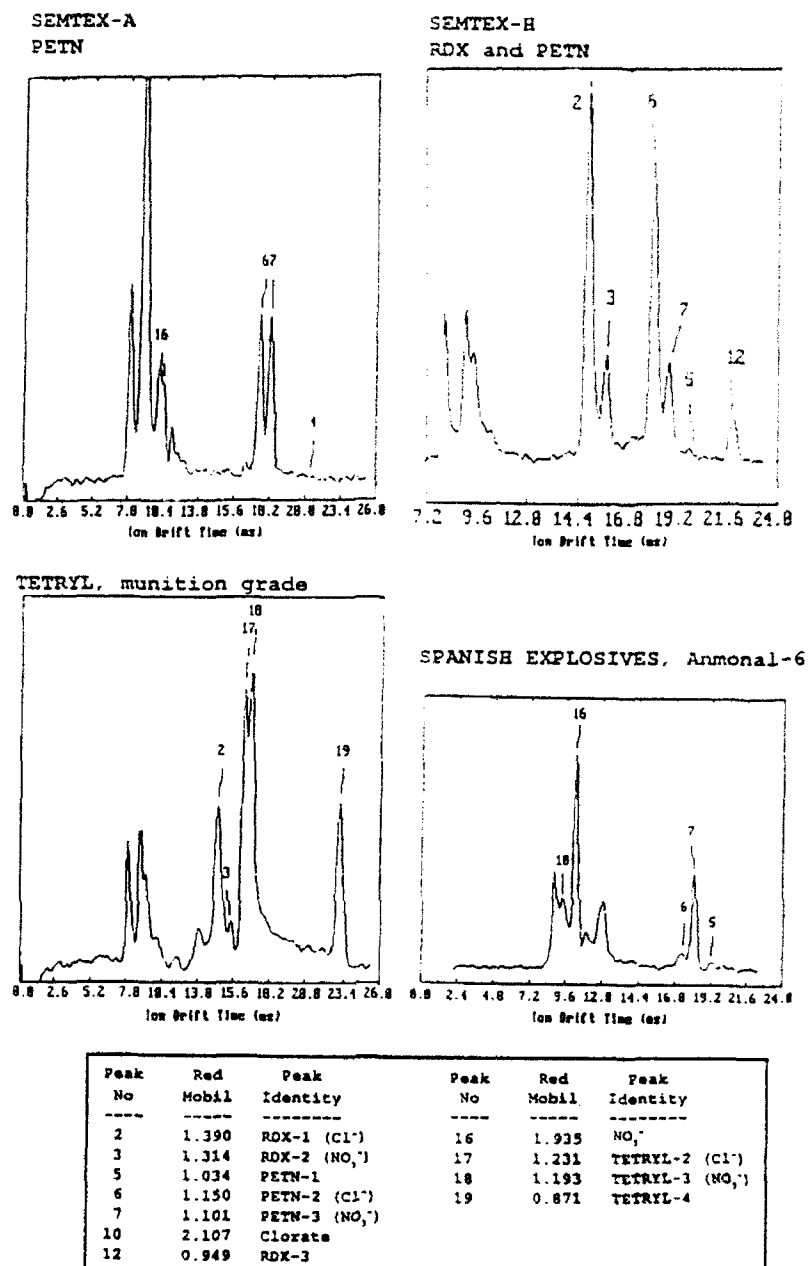


Figure 6. IONSCAN Plasmagrams of SEMTEX-A, SEMTEX-H, Tetryl and ANMONAL-6 Explosives

Table 4

IONSCAN Analysis of Commercial Explosives

<u>Commercial Explosive</u>	<u>Country of Origin</u>	<u>Explosive Components Detected</u>						
		<u>RDX</u>	<u>PETN</u>	<u>TNT</u>	<u>NG</u>	<u>EGDN</u>	<u>NO₃⁻</u>	<u>ClO₄⁻</u> ¹
C4	USA, Canada	X						
Deta Sheet	USA, Canada		X					
Semtex-A	Czechoslovakia		X					
Semtex-H	Czechoslovakia	X	X					
Plastrite	France		X					
Dynamite					X	X		
Water Jell							X	
IED ²	Spain	X	X	X			X	X

¹ May possibly be SO₃⁻; identification requires IMS/MS analysis.

² Components found in about 10 samples of Improvised Explosive Devices; all components are not present in all samples.

Under IONSCAN conditions, explosives (and taggants) form multiple ions -- for example, by proton abstraction, (M-H)⁺, and by addition of chloride, M.Cl⁺, and nitrate ions, M.NO₃⁺. The reactant, a chlorinated hydrocarbon in the IONSCAN carrier gas, is the source of chloride ions. Nitrate ions originate from the explosives themselves or from tropospheric NO_x contamination, particularly prevalent near airports. The relative intensities of the multiple ion peaks are influenced by concentration effects, by the stability and composition of commercial explosives, and by progress through the IONSCAN desorption cycle. In some situations, the relative intensities of peaks are dramatically reversed, and in others some previously strong peaks are completely suppressed. A thorough understanding of these intensity effects is essential for reliable explosives detection, and for the development of detection software to accommodate or take advantage of these effects.

The M.Cl⁺ and M.NO₃⁺ ion peaks are separated by less than 1 ms. In pure explosives, under IONSCAN conditions, M.Cl⁺ is usually the stronger peak, and M.NO₃⁺ may only appear as a poorly resolved shoulder; see RDX, PETN, Tetryl and HMX plasmagrams in Figure 5. In commercial explosives, the intensity of the M.NO₃⁺ peak often increases and may be comparable to that of the M.Cl⁺ peak; see Semtex-A, -H and munition-grade Tetryl plasmagrams in Figure 6. In commercial explosives that also contain ammonium nitrate, chloride ions are suppressed, and M.NO₃⁺ becomes the strongest or only peak for the explosive component M, but the nitrate ion, NO₃⁻ peak from ammonium nitrate will also usually be evident at lower drift times; see Spanish explosive plasmagram in Figure 6. This latter situation can also be simulated by spiking a substrate containing pure explosives with either ammonium nitrate or nitric acid; see RDX and Tetryl plasmagrams in Figure 5.

The above effects are due to varying amounts of nitrate ion in the ionization/reaction chamber. Nitrate ions compete effectively with chloride ions in the IMS ionization process because the nitrate electron affinity (3.9 eV) is higher than that of chloride (3.6 eV), and nitrate concentrations

can be high. In commercial explosives containing ammonium nitrate, formation of $M.Cl^-$ is completely suppressed. In commercial explosives with no ammonium nitrate, the higher nitrate ion concentration is due to thermal explosives decomposition. This instability appears to be higher in commercial formulations than in the pure explosive, particularly for PETN-containing explosives.

The relative intensities of the higher drift-time $M.(M.Cl)^-$ and $M.(M-MO_2)^-$ ion peaks, present in the plasmagrams of some explosives, also vary. For obvious reasons, they only appear when a relatively high concentration (nanogram range) of explosive is present in the sample.

Detection algorithms were developed to take account of the multiple-peak nature of many explosives, and to accommodate their varying relative intensities. These included multiple-peak criteria, for example, 2 of 3 known peaks must be present for a "hit", and detection criteria for different situations, for example, presence of nitrate ion in either high or low concentration. Both types improve detection reliability and reduce false alarm rates (FAR).

The relative intensities of peaks also vary as the IONSCAN analysis progresses. An IONSCAN analysis lasting 4-5 s consists of several analysis windows, each corresponding to a discrete time portion of that 4-5 seconds, and with each window being the sum of several 20-25 ms scans. Figure 7 shows how the relative intensities of EGDN and NG peaks vary during analysis of Forcite-40 dynamite. Peak growth characteristics are influenced by vaporization and ionization factors. For example, peaks of the more volatile EGDN appear early in the analysis cycle, and the EGDN $M.Cl^-$ peak growth is earlier than the corresponding $M.NO_3^-$ peak.

Peak growth characteristics are not a factor in an actual IONSCAN analysis since all windows are evaluated by the software. However, plasmagrams used for illustration in this report represent only one window of an analysis. The additional time-based information in the various windows of analysis may be used to develop algorithms to improve peak detection reliability, specifically as a means of resolving overlapping peaks.

3. Sampling Optimization

A number of different approaches to particulate sample collection and concentration have been developed and evaluated:

- * a cyclone which preconcentrates particles down to 1 micron,
- * a high flow rate (400-1000 litre/min) vacuum impactor,
- * direct suction through a porous substrate,
- * swiping surfaces with a paper tissue, followed by direct desorption,
- * use of a cotton glove, followed by transfer to an IONSCAN sampling substrate by direct suction through a porous substrate.

The first three methods use vacuum suction in conjunction with brushing. The fourth and especially the fifth method, which do not use suction as a primary sample collection technique, are finding increasing favour in Europe and the Middle East. However, it is impractical for high volume screening of passengers at airports.

Initially particle preconcentration was achieved using a cyclone and considerable effort was expended on characterising, interfacing and testing this device. Although effective, it was prone to contamination and clogging, and accordingly the construction and testing of alternative prototypes based on the impactor and flow-through approach were initiated.

The impactor was an efficient collector of particles greater than 10 microns, but it failed

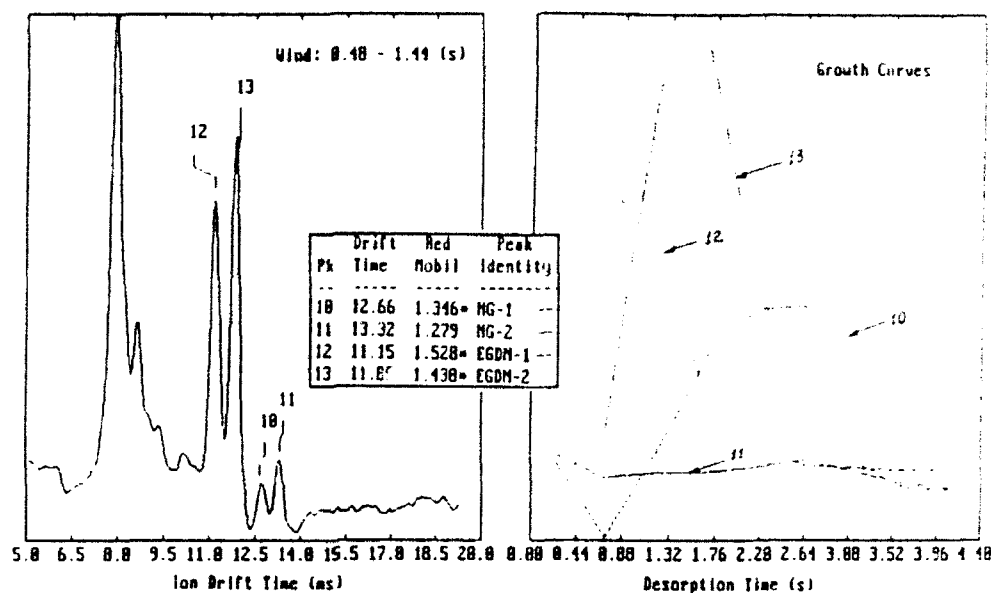


Figure 7. IONSCAN Plasmagram and Ion Growth Curves for Forcite-40 Dynamite

completely to collect micron and submicron particles. Also, the high air flow stripped the more volatile explosives, such as TNT and DNT, from the preconcentrated particles, and consequently these explosives were not available for detection in the IONSCAN.

A flow-through particle collection approach proved to be the most effective and simplest method for continuous in-line sample collection, in combination with a reel-to-reel tape drive system. An IONSCAN model 150 with a reel-to-reel tape drive system, Figure 8, was manufactured and has been used for tests at L.B. Pearson International (Toronto) airport.

Brush length, hose dimensions and flow rates were optimized, in conjunction with a porous teflon tape, selected for continual (ten pieces per minute) sampling. The porosity and flow rates for discrete and continual sampling are compared in Table 5.

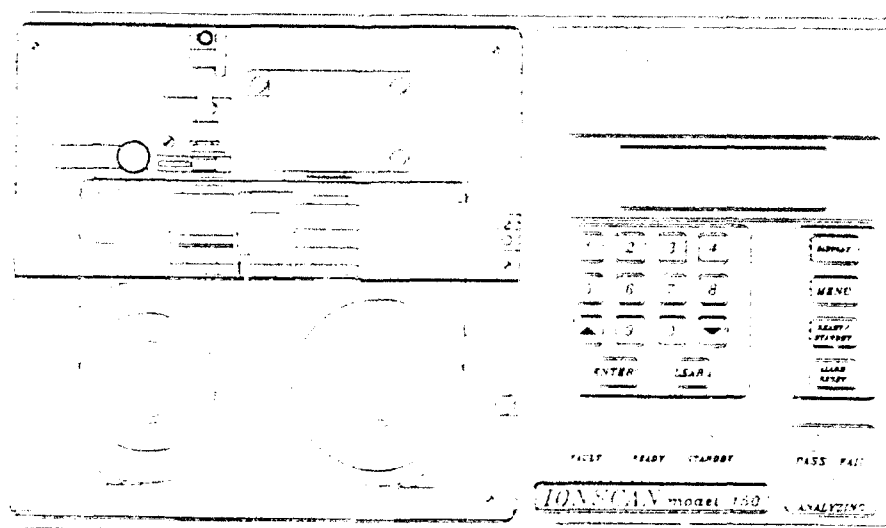


Figure 8. IONSCAN Model 150, Designed for Continual In-line Sampling



Figure 9. Continual Sampling System in Use

Table 5
Properties of Discrete and Continual Samplers

<u>Collection System</u>	<u>Porosity (microns)</u>	<u>Flow (L/min)</u>
Discrete (Filter)	50	150
Continual (Tape)	25	50

Laboratory testing showed that the two systems had comparable collection and desorption efficiencies. Observed sensitivities of samples vapourized from tape and filter were equivalent.

4. False Alarm Rate Tests

An on-site test activity, authorized by the Director General Security and Emergency Planning, was carried out at Toronto International Airport in March 1992.

Test dates and approximate number of bags examined were March 9 (300), March 10 (350), and March 13 (400). Figure 9 shows an IONSCAN and tape drive sample collection in action at an airport.

Table 6 shows the IONSCAN explosives programming for the tests, alarm criteria, and false alarms (based on 1050 samples):

Table 6
Toronto Airport Test Results (1050 samples)

<u>Explosive</u>	<u>Programmed Channels</u>	<u>Alarm Criteria</u>	<u>False Alarms</u>
RDX	3	2	0
PETN	3	2	0
TNT	1	1	1
DNT	1	1	1

There were several single peak detections for RDX and PETN but no false alarms because of their 2 out of 3 alarm criteria.

In addition to the above 1992 Canadian tests reported in some detail, over 9000 bags have been scanned in airport terminals in United States and in Europe. Some of those tests were earlier and some later than the above-tabulated tests. These tests have been done with a variety of IONSCAN models over the past few years and by many different inspection persons. Tests in 1990-91 had an inferior FAR to the current level. Improvements in FAR have been achieved in two ways. The software now identifies the baseline localized to the plasmagram peak, whereas in earlier software versions, the baseline was defined over a broad region of the plasmagram, which led to missed peaks and less accurate drift time measurements. Furthermore, an improved desiccant system has stabilized the water vapour content of the air introduced into IONSCAN over much

longer periods. This has permitted narrowing of detection "windows" from 100 to 50 μ s. As a consequence FAR values in controlled tests dropped to less than 0.5%.

Barringer has not been given complete details of many of those 9000 tests. However Barringer is assured by the inspection agencies involved in 1992 tests that the FAR is acceptably low, certainly less than 0.5 percent.

5. Acknowledgements

The authors acknowledge the financial and technical support of the United Kingdom's Home Office (Police Scientific Development Branch) and British Airport Authority, The United States' Federal Aviation Administration, and Canada's Transport Development Centre, Department of National Defence (Defence Industrial Research Programme) and National Research Council.

The contributions of many BRL scientists, engineers and technologists is gratefully acknowledged.

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PREDICTION OF THE LIFE-TIME OF A TAGGANT IN A COMPOSITION

R. A. REED, C. CAMPBELL, AND T. H. CHEN

*U. S. Army Armament Research, Development, and
Engineering Center Picatinny Arsenal, New Jersey
07806-5000, U. S. A.*

ABSTRACT. As part of our comprehensive tagging program, the life-time of a vapor taggant in a composition is being studied. Life-time is a critical parameter which ranks in importance only next to detectability. The objective of this paper is to apply the semi-finite linear diffusion model to predict the life-time of a vapor taggant in a composition. A long-term experiment is being conducted to study the loss of the vapor taggant as a function of sample thickness, temperature, and time. This paper will describe the theory and experimental design employed and discuss the applicability of the theoretical model to the experimental data obtained to date.

1. Introduction

For practical applications, a taggant in a composition must have an extended life-time. The latter is determined by the physico-chemical characteristics of both the taggant as well as the composition. In practice, the life-time measurement involves kinetic studies of the taggant loss from the composition as a function of temperature, time, and the boundary conditions of the samples, such as the sample geometry and the degree of freedom for taggant diffusion.

The objective of this paper is to undertake such studies involving a unique taggant in a plastic explosive composition.

2. Experimental

2.1. APPARATUS

Five Lab-Line Multi-Block Module Heaters Model 2050 capable of providing accurate temperature control with $\pm 0.50^{\circ}\text{C}$ uniformity were used in the heating of the control and tagged specimens. The sample containers were specially machined from a solid 1" aluminum rod (see Figure 1). Two small holes 180° apart were drilled near the top of the container to facilitate removal of the heated container from the heater for weighing. The sample was packed to 4.0 mm from the top of the container. Therefore, the depths of the three kinds of containers (10 each) were, respectively, 10.35 mm, 16.70 mm, and 29.40 mm. The latter were inserted into the holes of the heating blocks which are maintained at several different temperatures. In each heating block, a Chromel-Alumel thermocouple was inserted into the thermocouple well and the temperatures of all heating blocks were monitored continuously using a multistation digital temperature monitor.

A ternary high performance liquid chromatograph was used in the analysis of the taggant.

3. Results and Discussion

3.1. PREPARATION OF HOMOGENEOUSLY TAGGED COMPOSITION

In order to obtain valid results in the life-time studies, homogeneously tagged samples are required. Therefore, a simple procedure was devised to prepare such specimens. Further, in order to simulate a situation as close as possible to the "real

world", the modified plastic explosive compositions tagged with the taggant at nominally 1.0 and 0.1 wt. % concentrations were prepared using a two-pound scale manufacturing plant equipment.

A total of 50 pounds, i.e., 25 batches, each of control (untagged), tagged at 1.0 wt. %, and tagged at 0.10 wt. % compositions, were prepared.

A total of five cored samples were obtained from each of the 50 pound cubic blocks of tagged plastic explosive compositions containing approximately 1.0 and 0.10 wt. % taggant to determine the homogeneity of taggant distribution. The five samples represent the center-top, center-middle, and center-bottom along the vertical axis, left-side, and the right-side along the horizontal central axis. The samples were analyzed by the high performance liquid chromatographic method (HPLC) developed for this work.

The samples were found to be homogeneous within the experimental error and the concentrations were identical to the nominal values. Thus, the simple mixing process and equipment used enabled the preparation of homogeneous specimens without observable taggant loss.

3.2. THEORY

Equation (1) used in this work was obtained by integration of Equation (24) in Reference 1.

$$Q_t/Q_o = (8/\pi^2) \sum_{k=0}^{\infty} \{1 - \exp[-(2k+1)^2 \pi^2 D t / 4 \partial^2]\} / (2k+1)^2 \quad (1)$$

Where Q_t is the concentration of the taggant at time t , Q_o is the initial concentration of the taggant, D is the diffusion coefficient of the taggant, and ∂ is the sample thickness.

3.3. FITTING OF PREDICTIVE MODEL TO EXPERIMENTAL DATA

Figure 2 shows the result of fitting Equation (1) to the taggant loss data obtained so far at 30 °C. The fitting is quite good. However, the model seems to predict a slightly greater taggant loss at the initial stages and a slightly lower taggant loss at longer periods. This will be carefully examined in our continued work as a slight deviation in the prediction could result in a significant life-time error, especially in the case of long life-time as in this instance. Further refinement of the model may be necessary.

The taggant loss data so far indicate that the life-time of the taggant in the composition under study will be satisfactory for the intended application.

4. Conclusion

The semi-finite linear diffusion model fits the experimental data for the taggant loss quite well. However, the slight deviations observed may require further refinement of the model for reliable prediction of the taggant life-time.

The taggant loss data so far indicate that the life-time of the taggant in the composition under study will be satisfactory for the intended application.

5. Reference

1. S. Gottesfeld and S. W. Feldberg, J. Electroanal. Chem., **194**, 1-10 (1985).

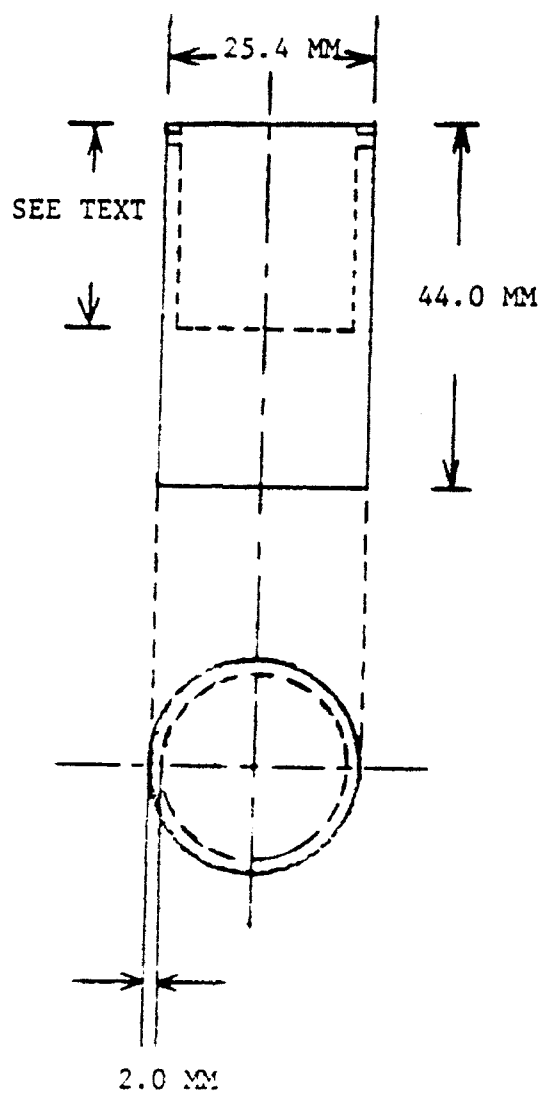


Figure 1. Diagram of Aluminum Sample Container

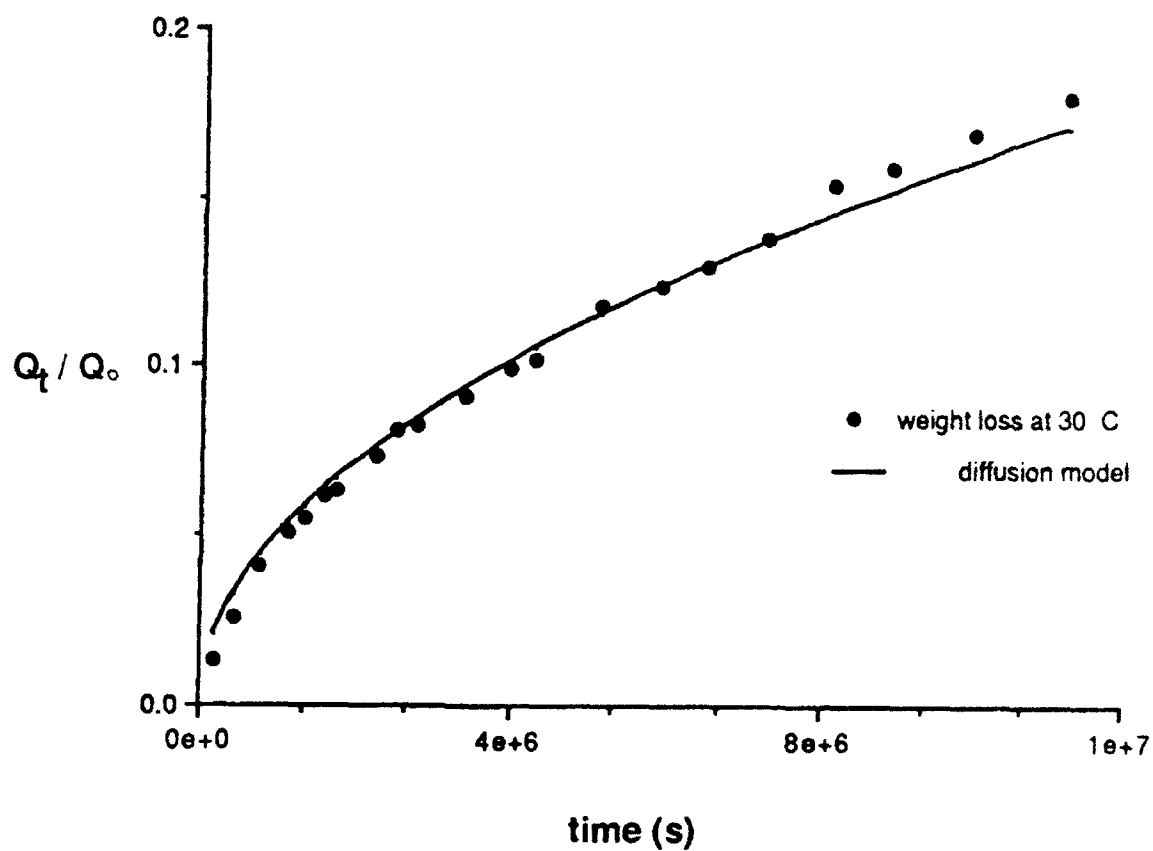


Figure 2. Fitting of Predictive Model to Experimental Data at 30 °C

ANALYSIS OF SEMTEX EXPLOSIVES

JOHN R. HOBBS

Volpe National Transportation Systems Center
Research and Special Programs Administration
U. S. Department of Transportation
Kendall Square
Cambridge, MA 02142 USA

ABSTRACT. Samples of the explosives Semtex H and Semtex A were analyzed to determine their composition and trace components. One Semtex H sample contained numerous impurities; the other Semtex H and Semtex A samples were uncontaminated. The results of these analyses underscore the need to analyze any explosives that are to be used for the evaluation of explosives vapor detectors.

1. Introduction

In a recent test of explosives detecting dogs, a 2 pound sample of Semtex H explosive was concealed in a large garage. As part of the testing protocol, samples of each explosive used in the test were examined by the Volpe Center for nitroglycerine (NG) and ethylene glycol dinitrate (EGDN) contamination, using the Scintrex Model EVD-1 explosives detector. This detector operates by analyzing vapors, trapped on a small Tenax cartridge, by thermal desorption and gas chromatography with electron-capture detection. In the course of setting up the detector, a sample of room air was taken and an enormous response for NG and EGDN was obtained. The Semtex H sample was then sampled with a Tenax trap and was found to be badly contaminated with NG and EGDN. Subsequent analysis of the bulk explosive by capillary gas chromatography with electron-capture detection (Figure 1) indicated the presence of ten electron capturing compounds in addition to the main ingredients of PETN and RDX [1]. The headspace vapors were trapped on a Tenax cartridge and were analyzed by capillary

gas chromatography with electron-capture detection and the results are shown in Figure 2. Large quantities of NG, EGDN, 2,4-DNT, and TNT were present. These results raised the question whether all samples of Semtex explosives contained this contamination. Therefore, samples of Semtex explosives were obtained from a different source and analyzed for trace and bulk components.

2. Explosive Samples

The Semtex H and Semtex A samples were provided by the Federal Aviation Administration Technical Center and were obtained from the Scientific Research and Development Branch, Home Office, England.

3. Analytical Methods

3.1 ANALYTICAL INSTRUMENTATION

The headspace method has been described previously [1]. GC-TEA headspace chromatograms were obtained for each sample.

A Hewlett Packard 5890 gas chromatograph was used with both the Hewlett Packard 5970B Mass Selective Detector (GC-MS) and with the Thermo Electron Thermal Energy Analyzer (GC-TEA). The samples were introduced into the gas chromatographs through a split/splitless injector operated in the splitless mode. The column used with both chromatographs was a 30 m J & W Scientific DB-5, held at 40 ° C for ten minutes, temperature programmed to 145 ° C at a rate of 10 ° C/min, and finally held at 145 ° C until the chromatography run was completed. Samples containing the dyes and oils were run on the same column held at 70 ° C for 4 minutes, temperature programmed to 270 ° C at a rate of 15 ° C /min, and finally held at 270 ° C for 10 minutes.

The Hewlett Packard 5970B Mass Selective Detector was operated in the scanning mode and operated under conditions provided by daily autotunes using perfluorotributylamine (PFTB). The resulting chromatography peaks were identified by performing a forward/backward library search of the NBS Mass Spectral Library Data Base for each background subtracted mass spectrum.

The Thermo Electron Thermal Energy Analyzer (TEA) was operated at 0.8 Torr, pyrolyzer temperature of 800 ° C, and interface temperature of 250 ° C. The high pyrolyzer temperature insured that compounds such as TNT are thoroughly converted to nitric oxide. The output of the TEA was filtered by a Spectrum 1021A filter-amplifier and from there to an analog input board of the gas chromatograph and from there to the Hewlett Packard gas chromatography data system for processing.

Fourier transform infrared spectra were obtained on a Perkin Elmer Model 1600 Fourier Transform Infrared (FTIR) Spectrometer using a KBr window cell.

3.2 SAMPLE PREPARATION

Approximately 1 gram of explosive was accurately weighed into a small container and extracted with 8 x 3.0 ml aliquots of hexane to remove all the hydrocarbons present. The residue from the extraction was dried and reweighed. The residue was then extracted with 8 x 3.0 ml aliquots of acetone to remove all explosives present. The residue was then dried and reweighed. The hexane extract contained the hydrocarbons which include the oil, dye, anti-oxidants, and the plasticizer. The hexane extract was then passed through a Waters silica Sep Pak. The Sep Pak retained the dye, plasticizer, and antioxidants, while the oil passed through with the hexane. The hexane was then analyzed by GC-MS to determine the oil type and then evaporated and the weight of the oil obtained. The Sep Pak cartridge containing the other hydrocarbons was flushed with 5 ml of methylene chloride to elute the remaining material, which was analyzed by GC-MS and FTIR. The Sep Pak was finally rinsed with 5 mls of acetone to remove any remaining material which was also analyzed by GC-MS. The first acetone extract of the bulk explosive was analyzed by GC-TEA to determine the ratio of PETN to RDX. The flow diagram of the separation scheme is shown in Figure 3.

4. Discussion of Results

4.1 HEADSPACE ANALYSIS

Figures 4 and 5 show the GC-TEA chromatograms of ninety minute headspace samples of Semtex H and A respectively. Compared to the 90 minute GC-TEA headspace chromatogram of the contaminated Semtex H

sample in Figure 3, these samples have very little headspace contamination. The peaks in Figures 4 and 5 have not been identified, but they are not due to cross contamination from other explosives, such as EGDN, NG, or TNT.

4.2 ANALYSIS OF EXPLOSIVE CONTENT

The GC-TEA chromatogram of the acetone extract of the Semtex H sample is shown in Figure 6. The explosives content is 49.8 % PETN and 50.2 % RDX. There is a small peak to the right of the main PETN peak; this appears to be a decomposition peak since the peak height of the right peak increased with temperature while the left peak height (PETN) decreased with temperature. Figure 7 is the GC-TEA chromatogram of the acetone extract of the Semtex A sample. Again, there is the decomposition peak of PETN and a trace of RDX. The explosives content is 94.3 % PETN and 5.7 % RDX.

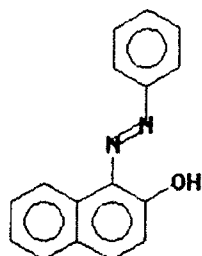
4.3 ANALYSIS OF OIL TYPE

Figures 8 and 9 show the Total Ion Chromatogram (TIC) of the hexane extracts from the Waters silica Sep Pak for Semtex H and A, respectively. The chromatograms are typical of low boiling paraffinic hydrocarbon oils and contain an unresolved, broad oil peak. An example of a low boiling hydrocarbon oil is mineral oil whose TIC is shown in Figure 10. For all practical purposes the TIC of all three oils are identical. Computer analysis of the peaks of the TIC of each oil indicates the presence of low boiling paraffinic hydrocarbons. The computer analysis of the TICs did not reveal the presence of any aromatic oils, such as naphthalenes, anthracenes, or phenanthracenes.

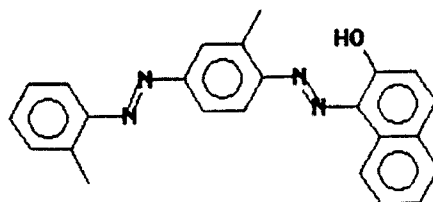
4.4 ANALYSIS OF DYES, PLASTICIZER, AND ANTIOXIDANTS

Figures 11 and 12 show the TICs of the methylene chloride extracts from the Waters silica Sep Pak for Semtex H and A, respectively. The peaks at 16.14 min. were identified as butyl 2-ethylhexyl 1,2-benzenedicarboxylic acid, as shown in the mass spectrum in Figure 13. As plasticizers are usually sebacates and phthalates, the compound is most likely bis(2-ethylhexyl) 1,2-benzenedicarboxylic acid (dioctyl phthalate), whose mass spectrum is shown in Figure 14. The peak at 18.36 min. was identified as N-phenyl-2-naphthalamine, whose mass spectrum is shown for comparison in Figure 15. N-phenyl-2-naphthalamine is a rubber antioxidant, known by its trade names Nonox DN and Nonox HP. The mass spectrum of the peak

at 20.56 min. in the TIC of Semtex H (Figure 11.) is shown in Figure 16. This peak is identified as 1-[(2,4-dimethylphenyl)-azo]-2-naphthalenol or Sudan I, the yellow dye. The structure of the Sudan I dye is shown below.



No peak in the TIC of the methylene chloride extract of Semtex A could be identified as a dye. The Fourier transform infrared spectra were taken of the extract and the potential suspect dyes Sudan II and Sudan IV. The spectrum of the extract is shown in Figure 17. The spectra from Sudan I and Sudan IV dyes were identical to the spectrum for the extract. A further search of peaks in the TIC of the methylene chloride extract identified a peak at 15.3 min. whose mass spectrum is shown in Figure 18 and is bis(2-methylphenyl)-diazene. Next, a GC-MS run was made of Sudan II and Sudan IV dyes. The TIC of Sudan II dye showed the expected mass spectrum for Sudan II dye, but the TIC for the Sudan IV dye did not reveal a peak for the parent dye Sudan IV. Instead, the TIC shown in Figure 19 revealed a peak at 15.3 min. whose mass spectrum is shown in Figure 20 and identified as bis(2-methylphenyl)-diazene. This would suggest that the dye in the Semtex A is Sudan IV and not Sudan II. Sudan IV dye is 1-[[2-methyl-4-[(2-methylphenyl)azo]phenyl]azo]-2-naphthalenol, whose structure is shown below.



Finally, the acetone rinse of the Waters Sep Pak, after the methylene chloride flush, revealed identical TICs for Semtex H and A, as shown in Figure 21. The mass spectrum of the single peak at 18.15 min. is shown in Figure 22 and is identified as butyl citrate, trade name Citroflex 4, which is a plasticizer and solvent for nitrocellulose lacquers, and is used in inks and polishes.

4.5 ANALYSIS OF BINDERS

Pyrolysis GC and infrared spectroscopy could have provided some information as to the nature of the binders, but these methods were not available. An attempt to determine the binders was made by "smoking", that is, lightly heating the residue from the extractions in a test tube and extracting the condensed smoke with methylene chloride for GC-MS analysis. Compounds identified in this analysis were 1-chloro-ethenyl-benzene, 2-ethenyl naphthalene (2-vinyl naphthalene), acetonitrile, 5-hexanenitrile, benzenebutanenitrile, benzonitrile, and benzene acetonitrile. According to the FBI laboratory, Semtex H contains styrene butadiene rubber, and pyrolysis GC reveals compounds such as styrene (ethenyl benzene), 1,3-butadiene, benzene, methyl benzene, dimethyl benzene, and methyl styrene. In pyrolysis GC the sample is heated in a helium atmosphere, while the "smoked" samples described above were heated in the presence of air and would most likely produce different compounds. Both Semtex H and A produced similar "smoked" TICs and compounds, and possibly both contain styrene butadiene rubber binders.

5. Summary of Results

The results of these analyses emphasize the need for information on chemical make-up of all explosives used for the evaluation of explosives detectors. The two Semtex H samples described in this paper are clear examples of explosives that could give different results when evaluating explosives vapor detectors. It is very important to determine if the samples are cross contaminated.

Table 1. summarizes the results of the analysis of the Semtex H and Semtex A samples. Table 2. lists the results of the gravimetric analysis.

6. Acknowledgements

The author wishes to acknowledge valuable discussions with Dr. Fred Whitehurst of the Federal Bureau of Investigation Laboratory and Mr. Ed Bender of the Bureau of Alcohol, Tobacco and Firearms Laboratory. The author would like to thank Mr. James Simms of the Massachusetts Institute of Technology Spectroscopy Laboratory for the Fourier transform infrared spectra. This work was funded by the Aviation Security Research and Development Service of the Federal Aviation Administration Technical Center.

7. Reference

- [1] Hobbs, John R., and Conde, E. (1989) 'Comparison of Different Headspace Techniques for the Analysis of Explosives', Proceedings of the 3rd International Conference on the Analysis and Detection of Explosives, Mannheim, FRG.

TABLE 1. Summary of Semtex Analysis

Component	Semtex H	Semtex A
% PETN	49.8	94.3
% RDX	50.2	5.7
Dye	Sudan I	Sudan IV
Antioxidant	N-phenyl-2-naphthalamine	N-phenyl-2-naphthalamine
Plasticizer	n-octyl Phthalate Butyl Citrate	n-octyl Phthalate Butyl Citrate
Binder	Styrene-butadiene rubber	Styrene-butadiene rubber

TABLE 2. Gravimetric Analysis

weights in grams	Semtex H	Semtex A
Sample Size	1.0194	1.1061
Weight oil	0.0811	0.0994
% oil by weight	7.9	9.0
Weight rubber	0.0920	0.1036
% rubber by weight	9.0	9.4
Weight acetone solubles	0.8156	0.8527
Weight explosives	0.7029	0.7029
% acetone solubles	86.2	82.4
Weight hexane solubles	0.1127	0.1498
% acetone solubles	13.8	17.6

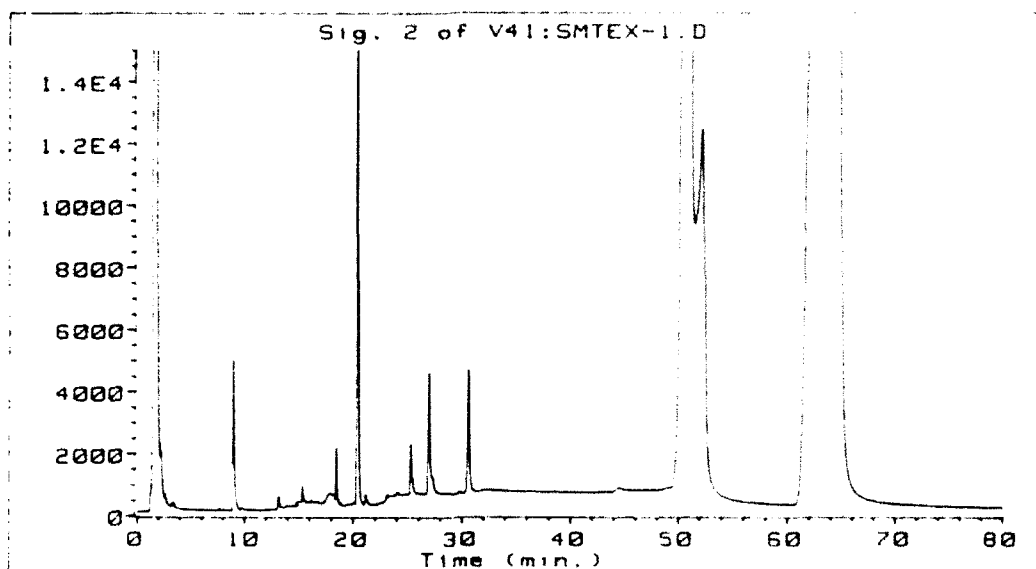


Figure 1. GC-ECD Chromatogram of Secret Service Semtex H.

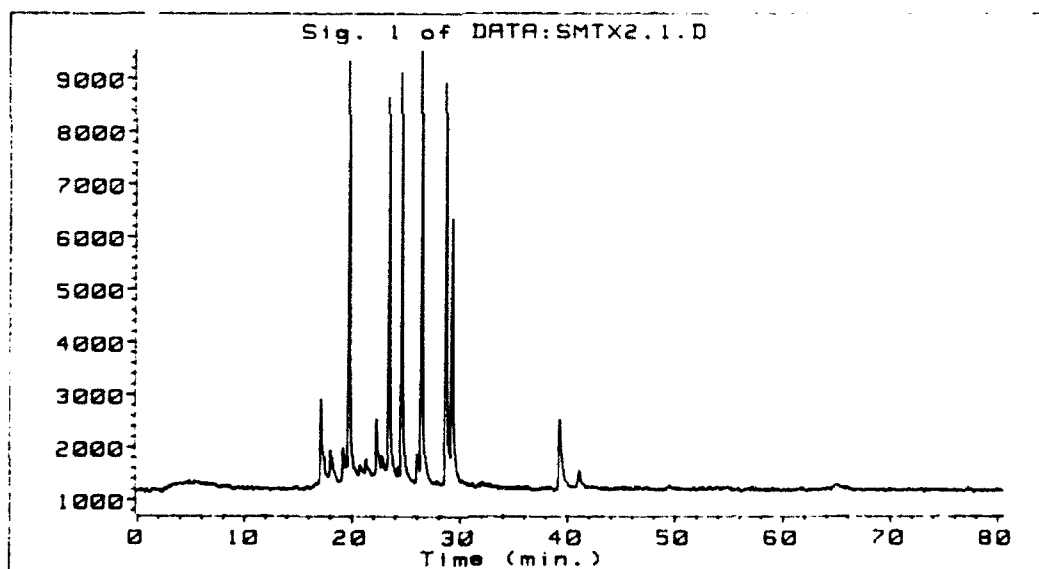


Figure 2. GC-TEA Chromatogram of 90 Minute Headspace of Semtex H.

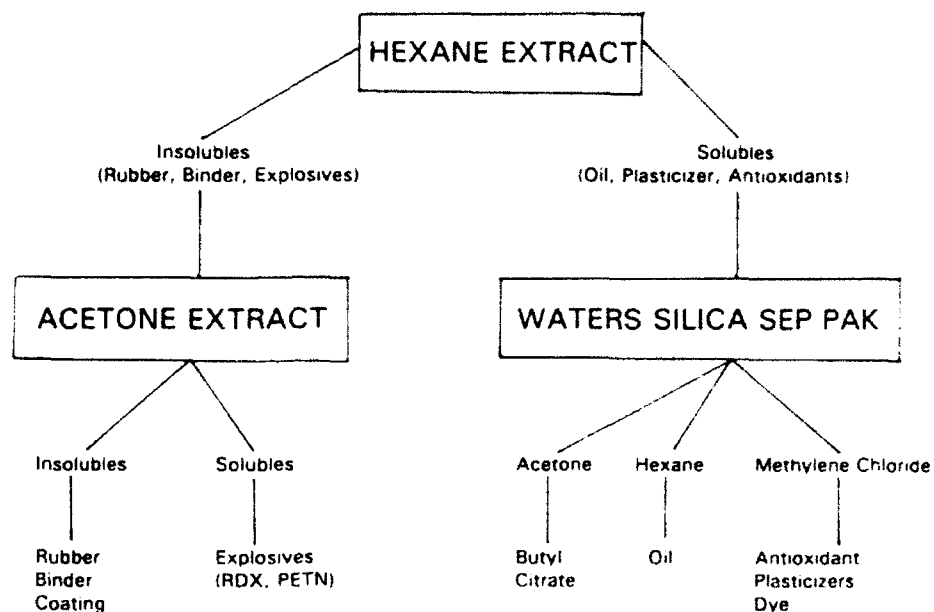


Figure 3. Analytical Separation Scheme.

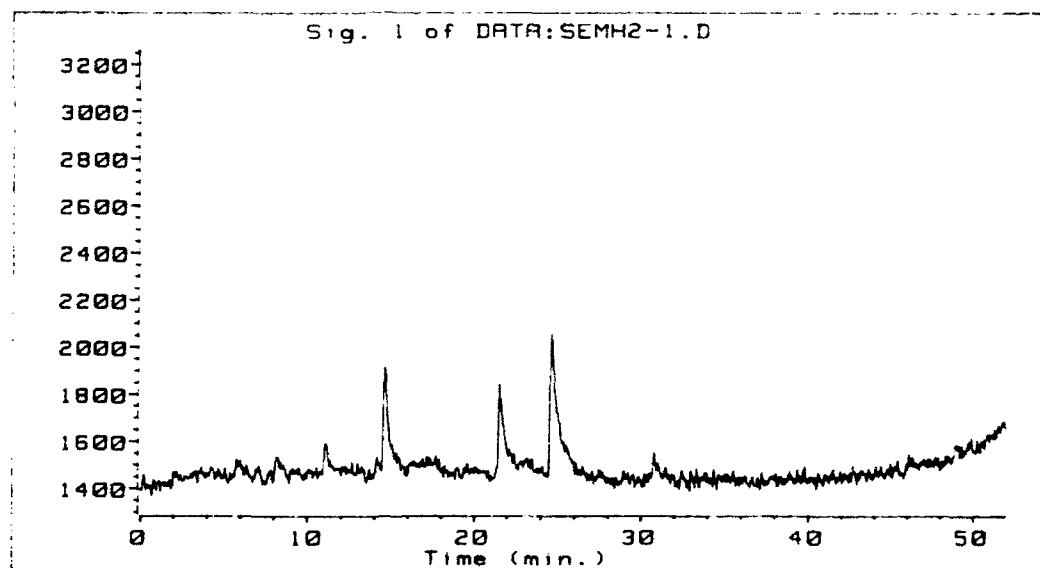


Figure 4. GC-TEA Chromatogram of 90 Minute Headspace of Semtex H.

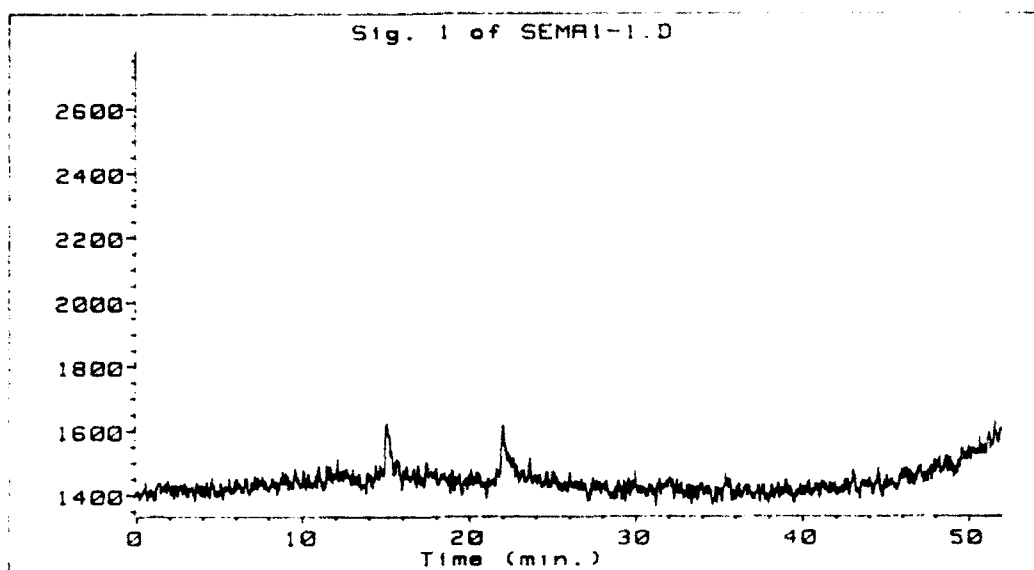


Figure 5. GC-TEA Chromatogram of 90 Minute Headspace of Semtex A

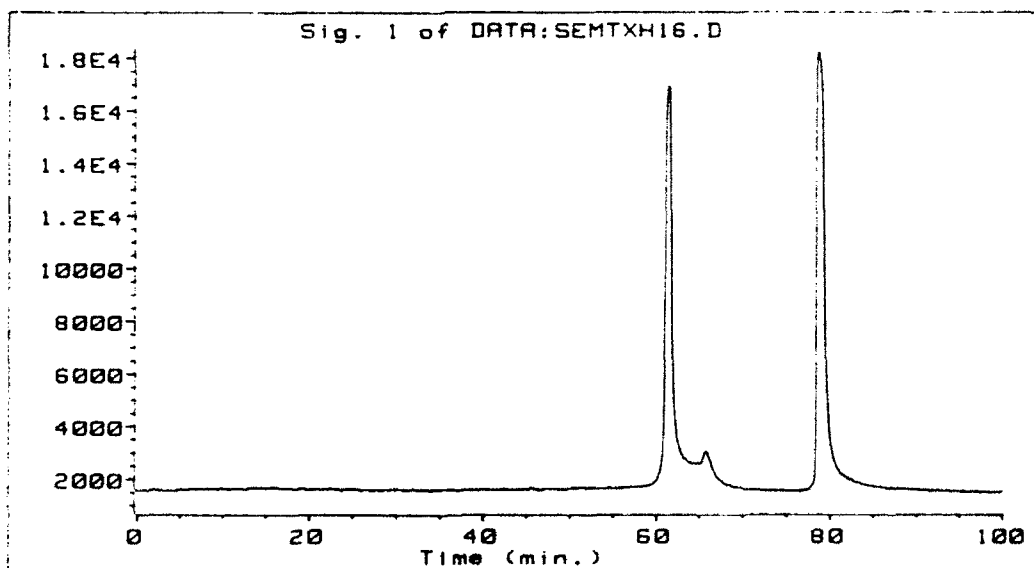


Figure 6. GC-TEA Chromatogram of Acetone Extract of Semtex H.

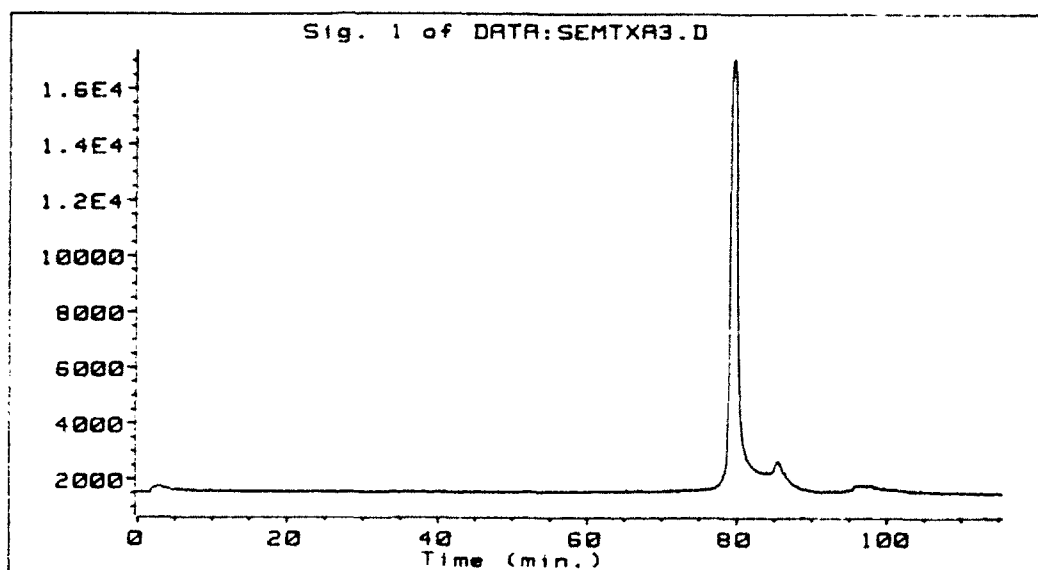


Figure 7. GC-TEA Chromatogram of Acetone Extract of Semtex A.

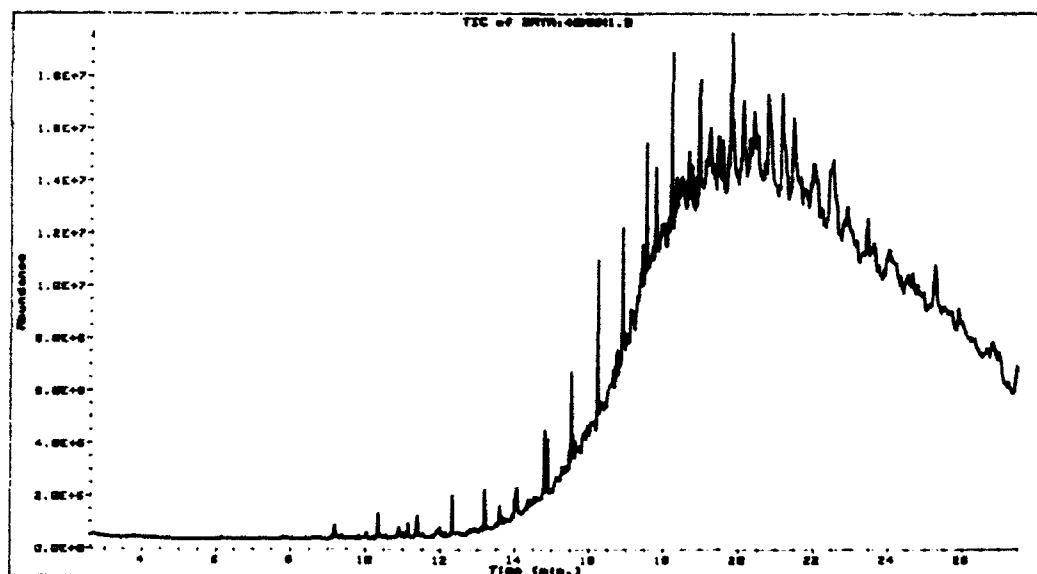


Figure 8. Total Ion Chromatogram of Hexene Extract of Semtex H from Sep Pak.

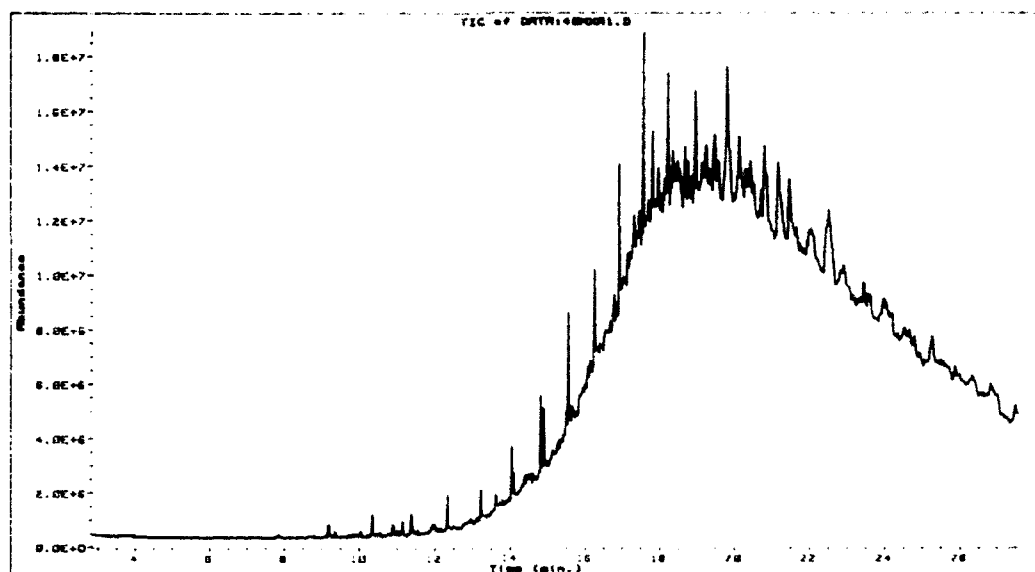


Figure 9. Total Ion Chromatogram of Hexane Extract of Semtex A from Sep Pak

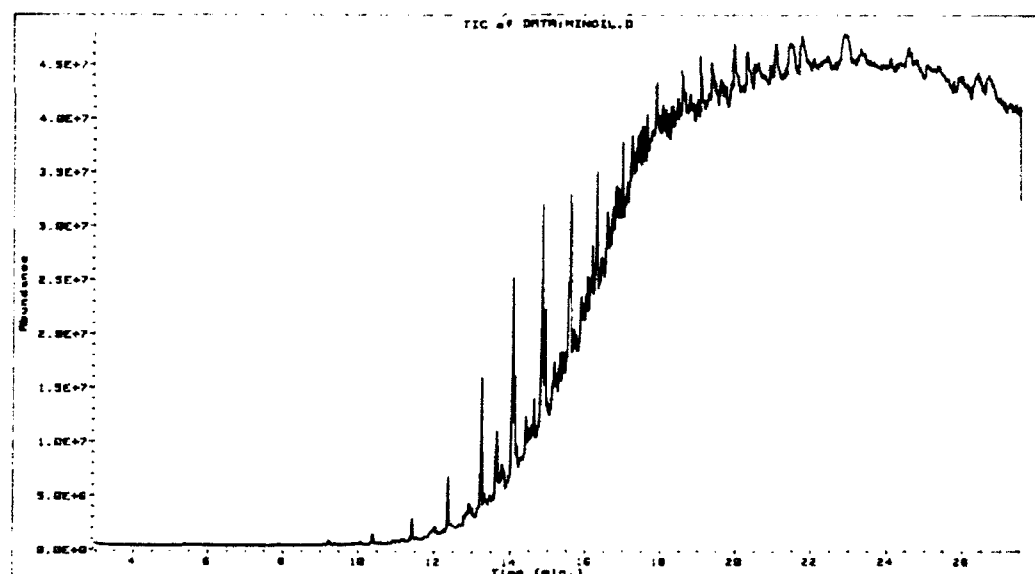


Figure 10. Total Ion Chromatogram of Mineral Oil.

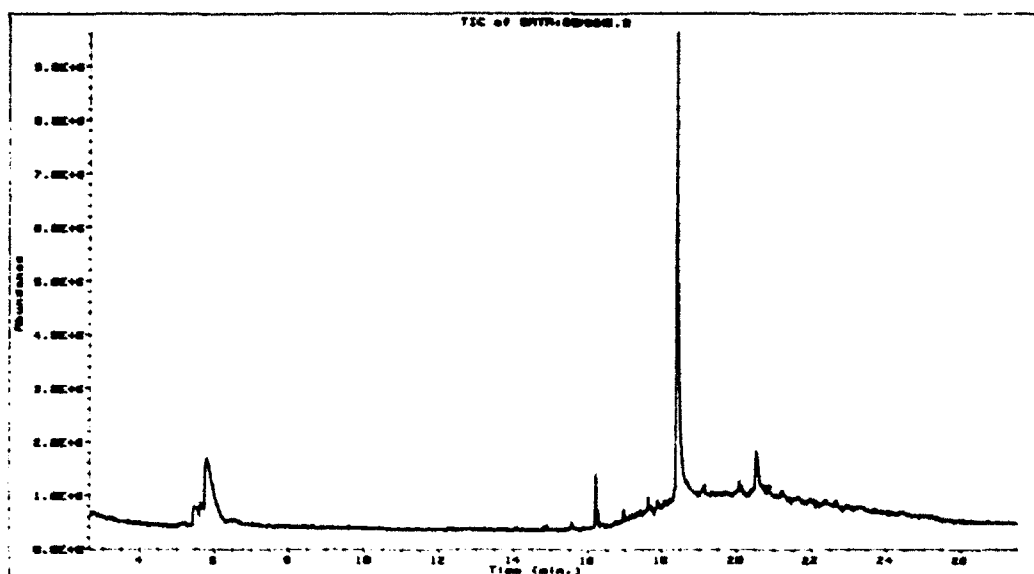


Figure 11. Total Ion Chromatogram of Methylene Chloride Extract of Semtex H from Sep Pak.

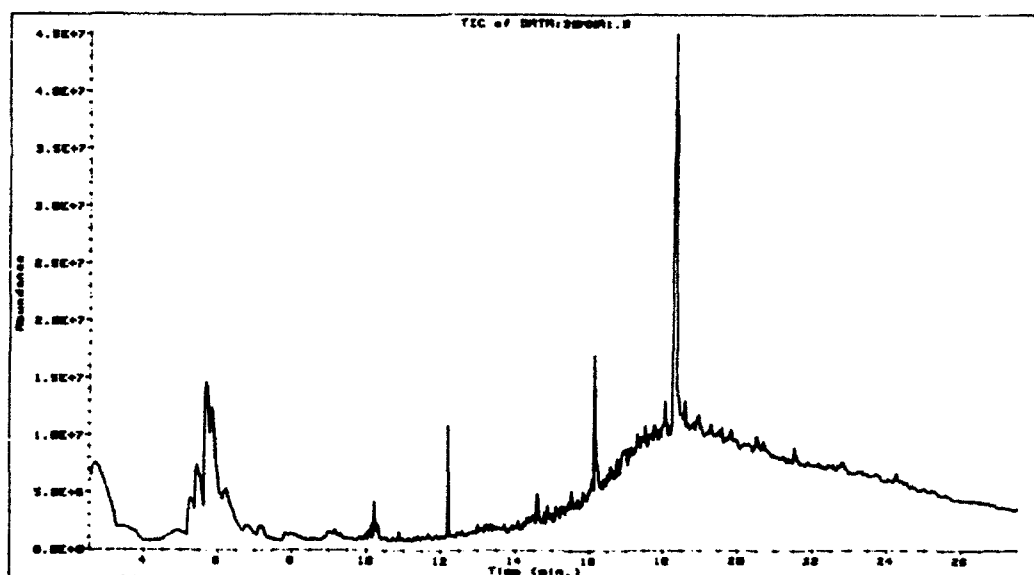


Figure 12. Total Ion Chromatogram of Methylene Chloride Extract of Semtex A from Sep Pak.

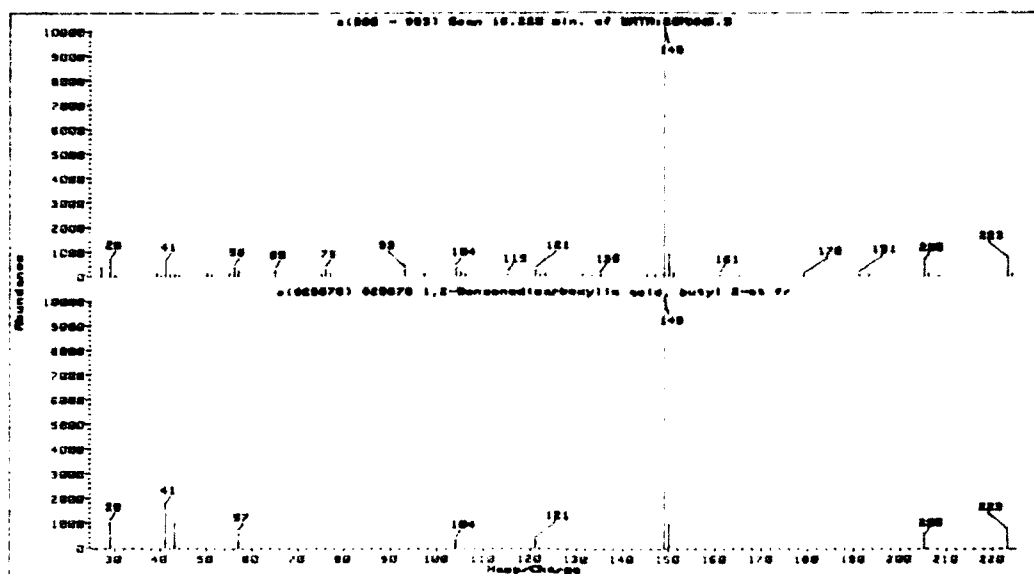


Figure 13. Mass Spectrum of Butyl-2-ethylhexyl-1,2-benzenedicarboxylic Acid.

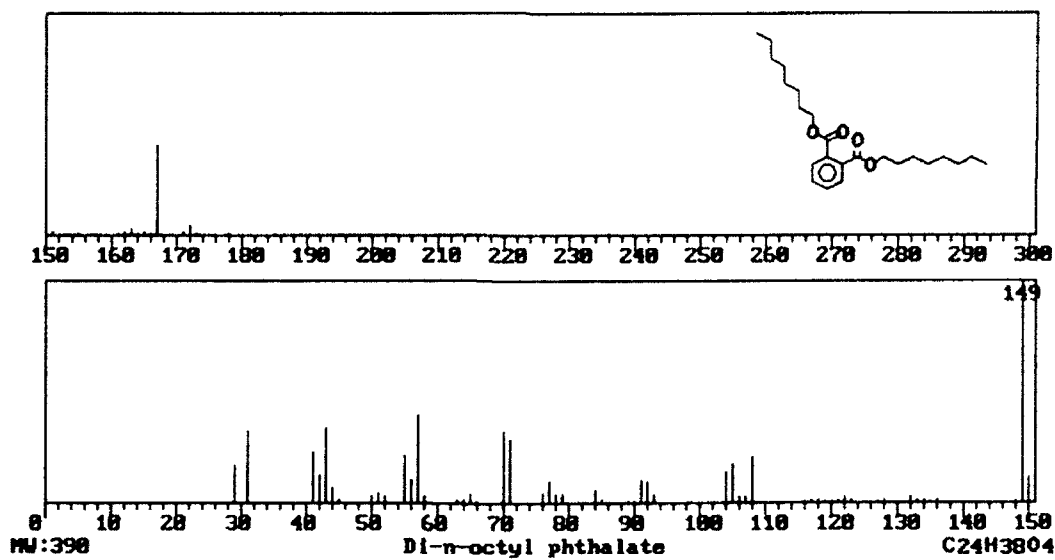


Figure 14. Mass Spectrum of Dioctyl Phthalate.

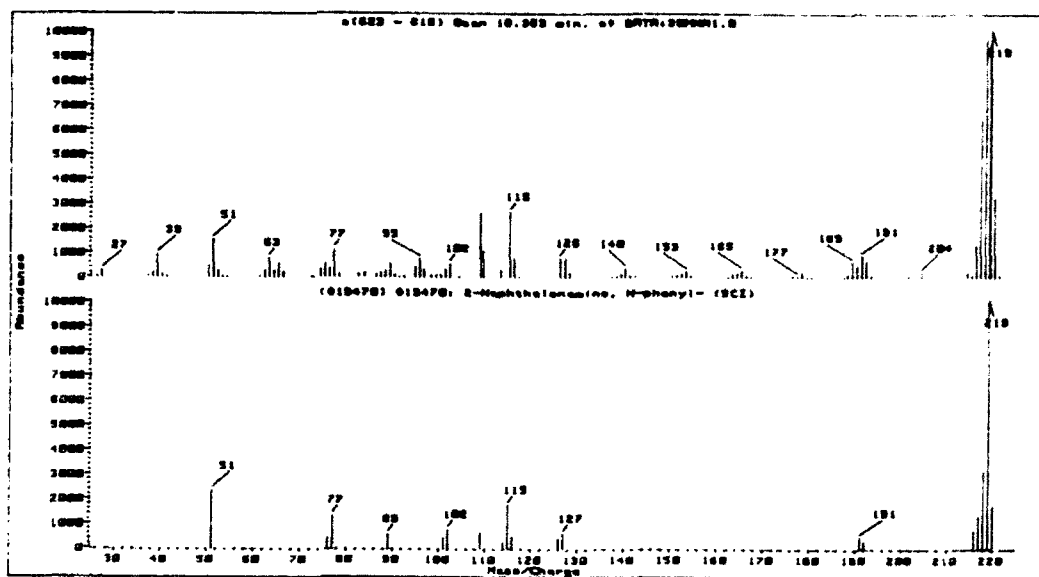


Figure 15. Mass Spectrum of N-Phenyl-2-Naphthylamine.

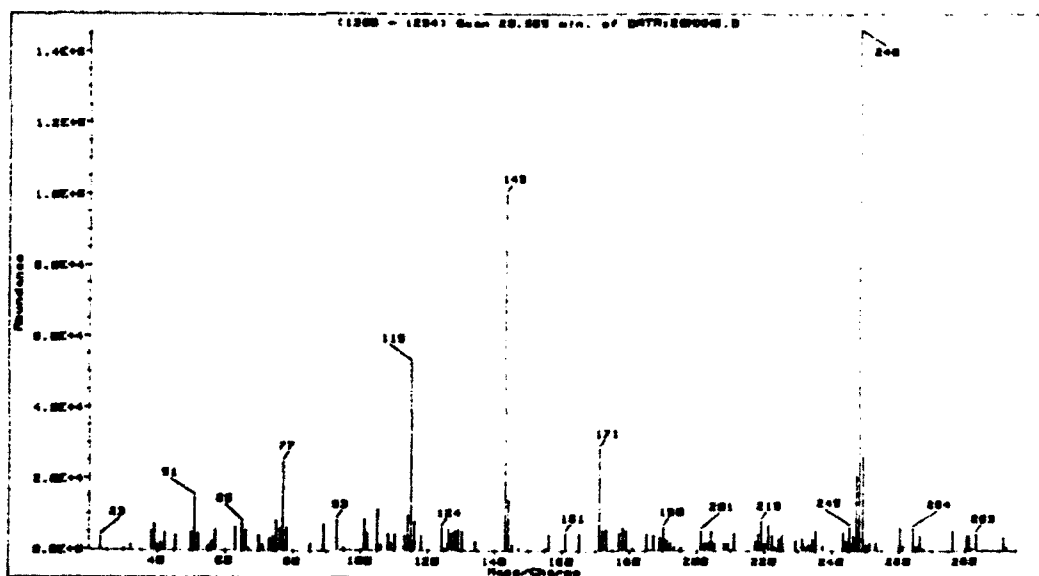


Figure 16. Mass Spectrum of Sudan I Dye.

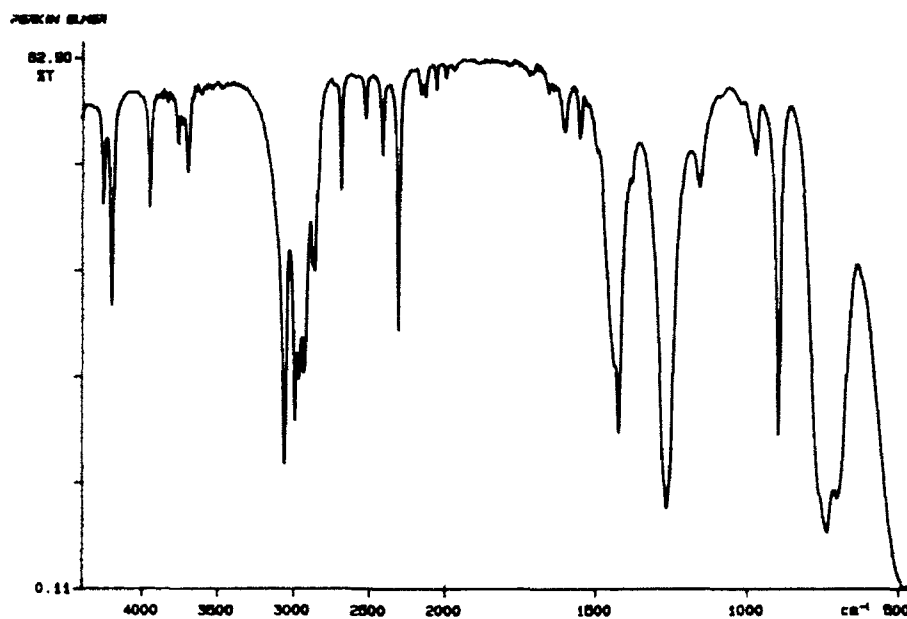


Figure 17. Fourier Transform Infrared Spectrum of the Methylene Chloride Extract of Semtex A

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Y: 4 scans, 4.0cm⁻¹

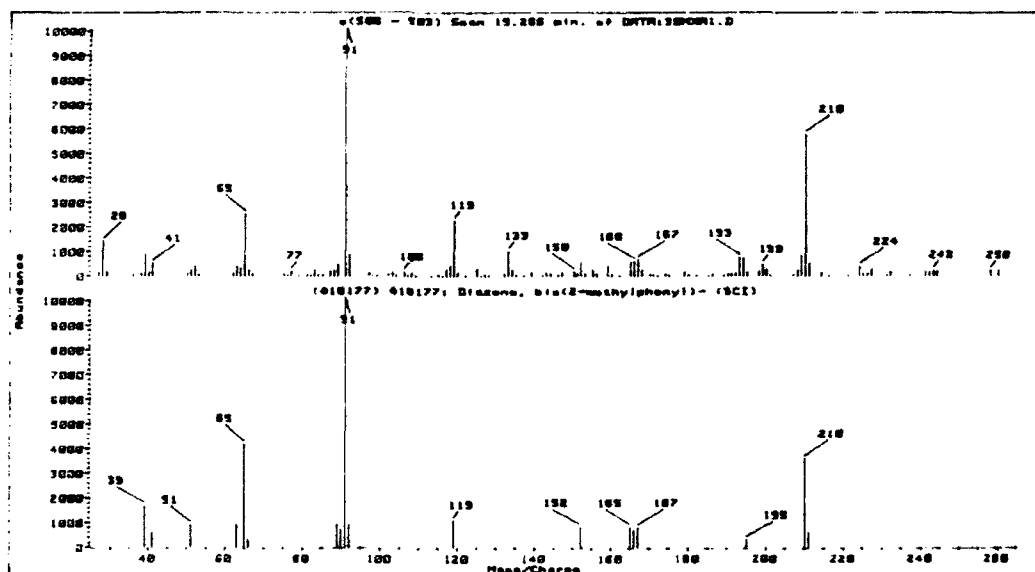


Figure 18. Mass Spectrum of Bis(2-methylphenyl)-Diazene.

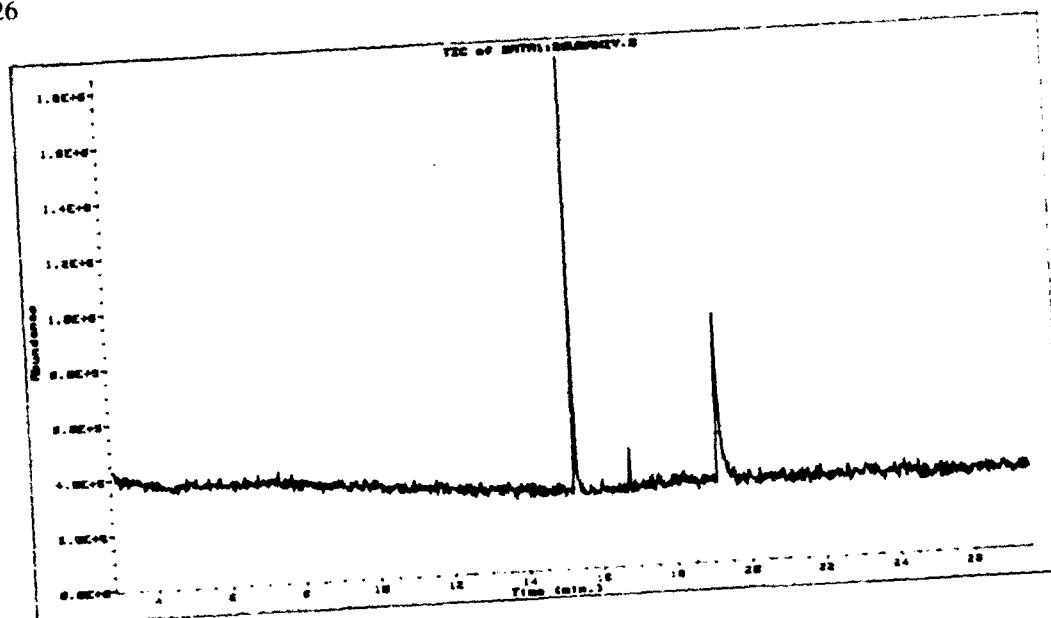


Figure 19. Total Ion Chromatogram of Sudan IV Dye.

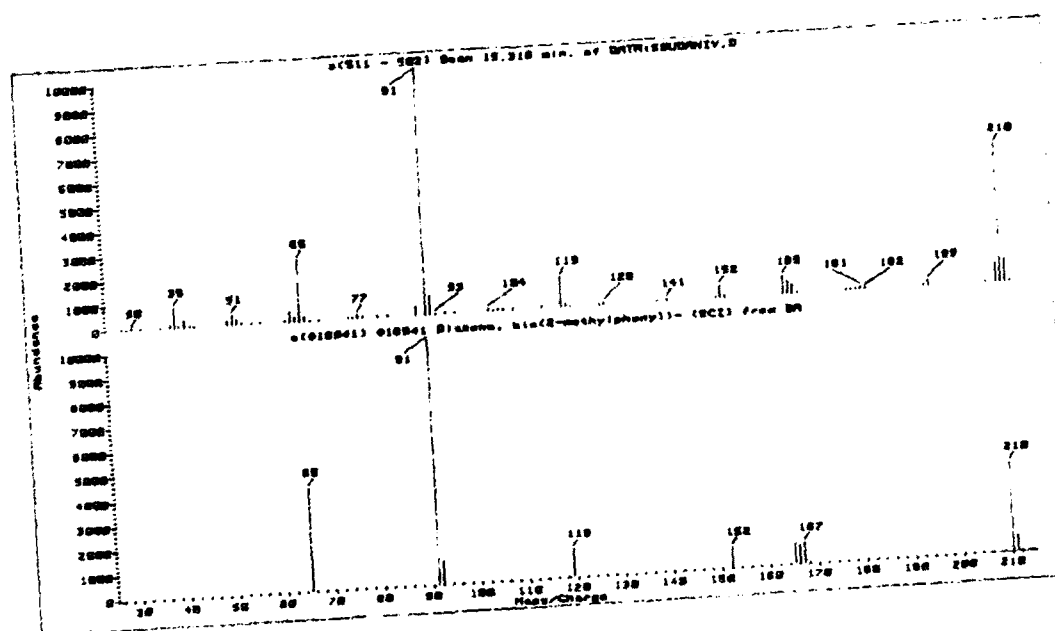


Figure 20. Mass Spectrum of Peak at Retention Time 15.3 Minutes of Sudan IV Dye.

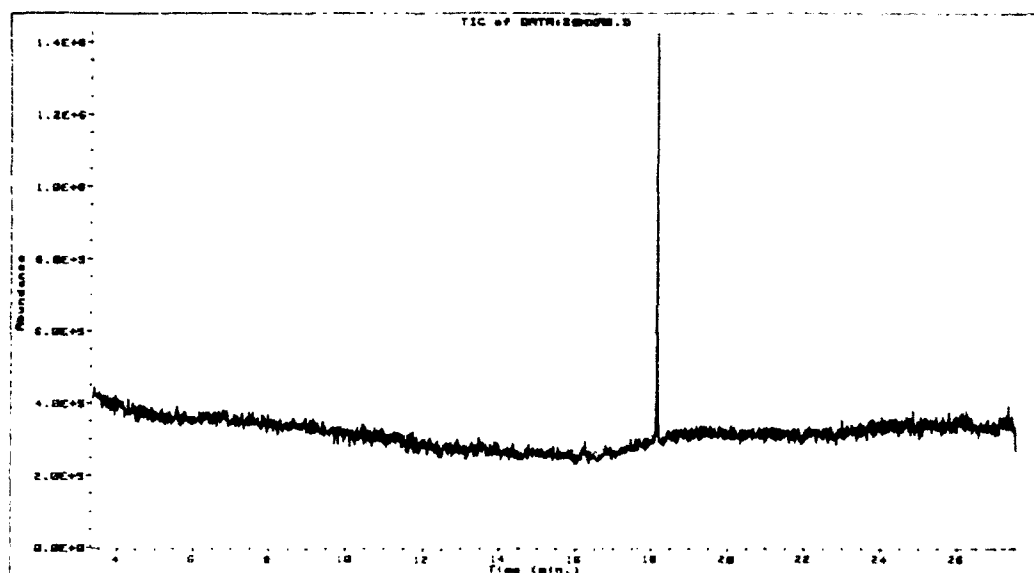


Figure 21. Total Ion Chromatogram of Acetone Extract from Sep Pak after Methylene Chloride Flush.

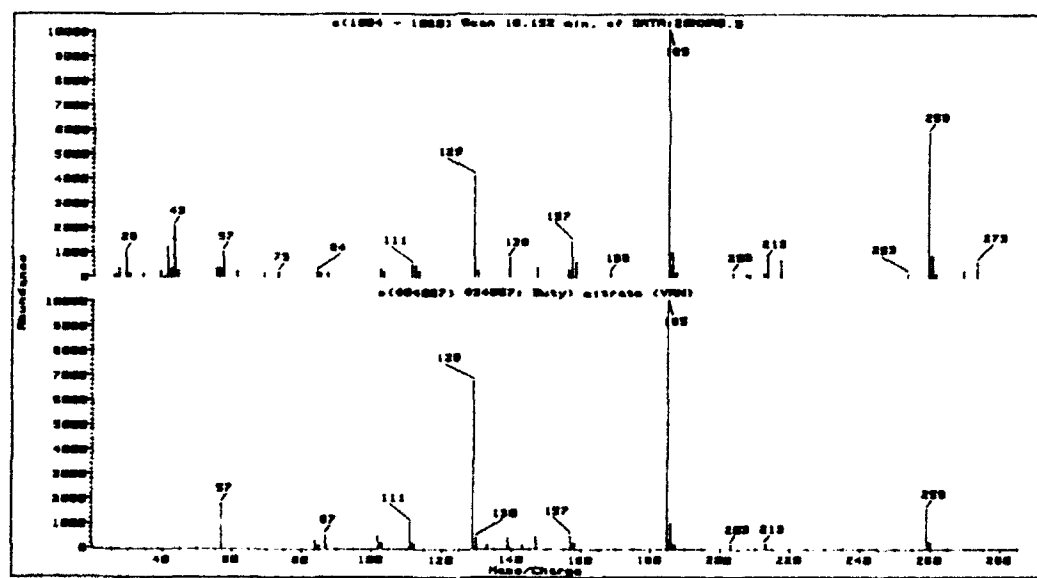


Figure 22. Mass Spectrum of Butyl Citrate.

CONSIDERATION OF SOME ASPECTS OF MARKING PLASTIC EXPLOSIVE SEMTEX

P. MOSTAK, M. STANCL, V. PREUSSLER
VCHZ Synthesia, VÚPCH
532 17 Pardubice-Semín
Czechoslovakia

ABSTRACT. A method for measuring the emission rate of marking agents was developed, and the emission of EGDN from marked plastic explosive SEMTEX was measured under various conditions. The fluctuation of emission rate of EGDN from marked plastic explosive SEMTEX 1A were estimated. The relation between the emission rate and the concentration of EGDN in SEMTEX 1A was studied. A comparison between the emission rate of EGDN from the SEMTEX 1A and the C-4 was made and possible explanation of differences in emission rate at these explosives was proposed. The emission rate of EGDN and DMNB from SEMTEX 1A was studied in an air stream at two different velocities. The possible mechanism controlling the emission rate is discussed.

1. Introduction

The emission rate of marking agents from plastic explosives is an important property of marked plastic explosives. Its value corresponds, in general, to the ability of explosive vapour detectors used to detect marked explosives. Therefore, a suitable method for the measuring of emission rates is vital. The application of such a method enables us to study some aspects of technological process for the production of marked plastic explosives and also to estimate the mass of marking agent which is emitted from the surface of explosive under various conditions. Some applications of the developed method are presented in this paper.

2. Method for Estimation of Emission Rate

The following procedure was developed for the estimation of the emission rate of marking agents from plastic explosives.

2.1. PREPARATION OF SAMPLE

A piece of explosive having dimensions of 7 x 1.5 x 1.5 cm is cut off from a block of plastic explosive. The explosive is transferred to a glass weighing cup, the excess explosive is cut off with a knife or a steel string. The surface of the explosive is to be smooth, the surface area being 8.6 cm².

2.2. SAMPLING APPARATUS

The sample is inserted in a glass tube of 2.5 cm in dia. and 13 cm in length. The glass tube is connected with 2 absorbers containing fritted glass inserts, a volume of each absorber being 20 ml. A 8 % methanol-water solution is used in the first absorber, distilled water in the second one. The absorbers are connected to a flowmeter and an air pump. The scheme of the sampling apparatus is shown in Figure 1.

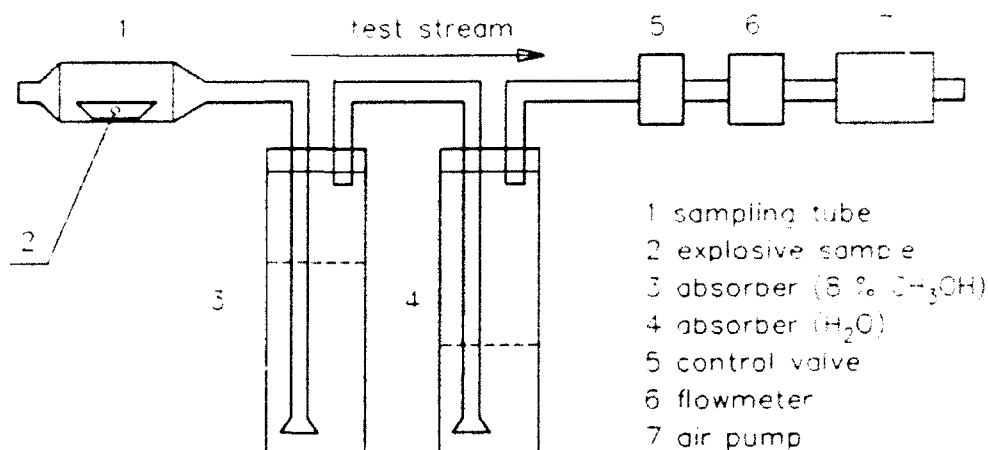


Figure 1. Sampling apparatus

2.3. SAMPLING PROCEDURE

The flow of air through the sampling apparatus is controlled at a level of 60 mlmin⁻¹, the time of sampling being 60 min, temperature 20 °C.

2.4. ANALYSIS OF ABSORBED VAPOURS

High performance liquid chromatographic method (HPLC) is used for the analysis of EGDN taken in the sampling apparatus.

The procedure is as follows:

- transfer the contents of both absorbers into a 50 ml volumetric flask and make up to the mark with distilled water
- pipette 5 ml stock solution prepared above into a 25 ml volumetric flask, add 10 ml of methanol solution of 1,3, 5-trinitrobenzene having a concentration 5×10^{-4} gml⁻¹ (inner standard) and make up to the mark with distilled water.
- inject 0.5 ml of the solution to a HPLC instrument using the following conditions:
 Column: Separon SGX C-18, 7 μ m, 3x150 mm, (Tessek Ltd. Prague)
 Detector: UV, 215 or 220 nm
 Mobile Phase: 45 % methanol
 Flow Rate: 0.5 mlmin⁻¹.
 Temperature: 20 °C

3. Emission rate of EGDN from marked SEMTEX

The emission rate of EGDN was measured at SEMTEX 1A marked by marking particles in the production line. Samples were taken from mixers at the end of mixing, each sample representing one mixer content. The quantity of marking particles corresponded to 0.2 % concentration level of EGDN in SEMTEX 1A. Results of experiments are summarized in Table 1.

Table 1 - Emission rate of EGDN from SEMTEX 1A

Sample	Emission rate ($\text{gcm}^{-2}\cdot\text{h}^{-1}\cdot 10^{-5}$)	Sample	Emission rate ($\text{gcm}^{-2}\cdot\text{h}^{-1}\cdot 10^{-5}$)
1	2.40	8	2.82
2	1.95	9	2.59
3	2.43	10	2.73
4	2.37	11	2.63
5	2.08	12	2.79
6	2.48	13	2.59
7	2.77	14	2.67

It can be concluded, that the fluctuation of emission rates is low, the mean value being 2.52×10^{-5} ($\text{gcm}^{-2}\cdot\text{h}^{-1}$), results confirm good reproducibility of marking. Than the emission rate of EGDN was measured after 6 days following the production. The results are shown in Table 2.

Table 2 - Emission rate of EGDN after 6 days

Sample	Emission rate ($\text{gcm}^{-2}\cdot\text{h}^{-1}\cdot 10^{-5}$)
1	3.96
2	4.18
3	4.11
4	3.21
5	3.63
6	3.74
7	3.89

The emission rate estimated 6 days after production is approx. 150 % of the value of fresh explosive. This fact is caused by the diffusion of EGDN from marking particles into product, this process is time dependent and some time is necessary to achieve the equilibrium of EGDN concentration in the whole mass of SEMTEX.

4. Relation of Emission Rate to Concentration of EGDN

The relation of the emission rate to the concentration of EGDN in SEMTEX 1A was studied in laboratory conditions. The emission rate and concentration of EGDN in explosive were estimated immediately after the preparation of marked SEMTEX 1A. Results obtained are summarized in Table 3 and Figure 2.

Table 3 - Emission rate at different concentrations of EGDN at SEMTEX 1A

Concentration of EGDN (%)		0.05	0.10	0.20
Emission rate $\text{gcm}^{-2}\cdot\text{h}^{-1}$	EGDN free	$1.64\cdot 10^{-5}$	$2.56\cdot 10^{-5}$	$4.55\cdot 10^{-5}$
	EGDN particles	$4.90\cdot 10^{-6}$	$1.16\cdot 10^{-5}$	$2.52\cdot 10^{-5}$

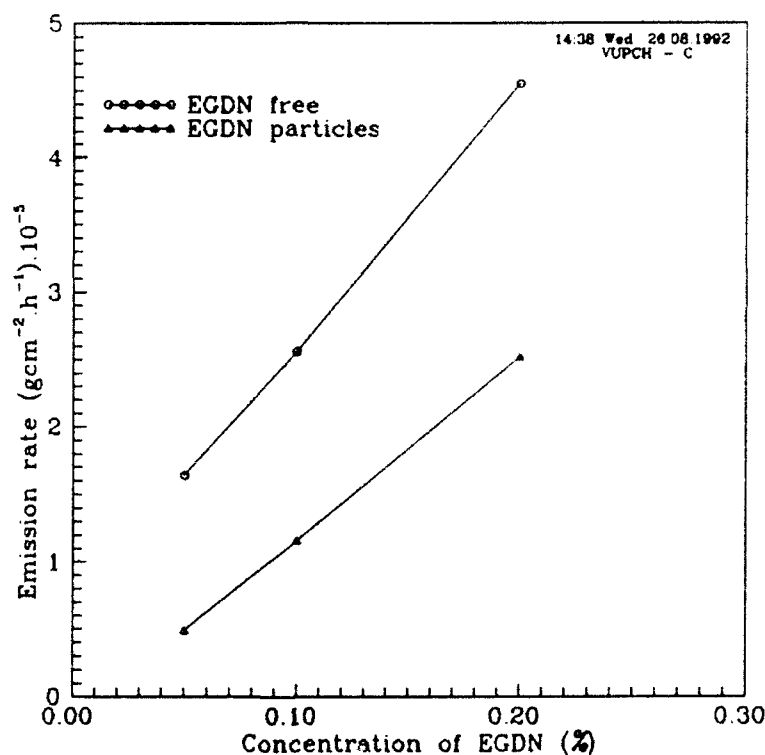


Figure 2. Relation of emission rate to concentration of EGDN at SEMTEX 1A

From the data obtained it is clear, that the relation of the emission rate to the concentration of EGDN is linear in this concentration range. Furthermore, the higher emission rate in case of free added EGDN can be seen when the fresh plastic explosive is studied.

5. Effect of Composition and Physical Properties of Plastic Explosives on Emission Rate

Possible changes in emission rates between different types of plastic explosives at the same concentration level of marking agent could affect the real probability of detection of individual plastic explosives. Therefore, the emission rate of EGDN from the plastic explosive C-4 was studied in comparison with SEMTEX 1A at a concentration level 0.2 %. EGDN was added to C-4 in a laboratory mixer both free and in marking particles. The change of emission rate in time is reported in Table 4 and Figure 3.

Table 4 - Emission rate of EGDN in C-4 and SEMTEX 1A

Days	Emission rate from SEMTEX 1A ($\text{gcm}^{-2}\cdot\text{h}^{-1}$) $\cdot 10^{-5}$		Emission rate from C-4 ($\text{gcm}^{-2}\cdot\text{h}^{-1}$) $\cdot 10^{-5}$	
	EGDN free	EGDN particles	EGDN free	EGDN particles
0	3.73	1.43	2.04	0.98
1	3.78	1.55	1.97	1.41
2	3.92	2.21	2.03	1.66
3	4.73	2.60	2.45	2.00
4	5.28	3.14	2.42	1.95
7	4.37	3.34	2.21	1.78
10	3.97	2.76	1.97	1.53
14	3.74	2.72	1.68	1.90
21	3.72	2.65	1.86	1.76

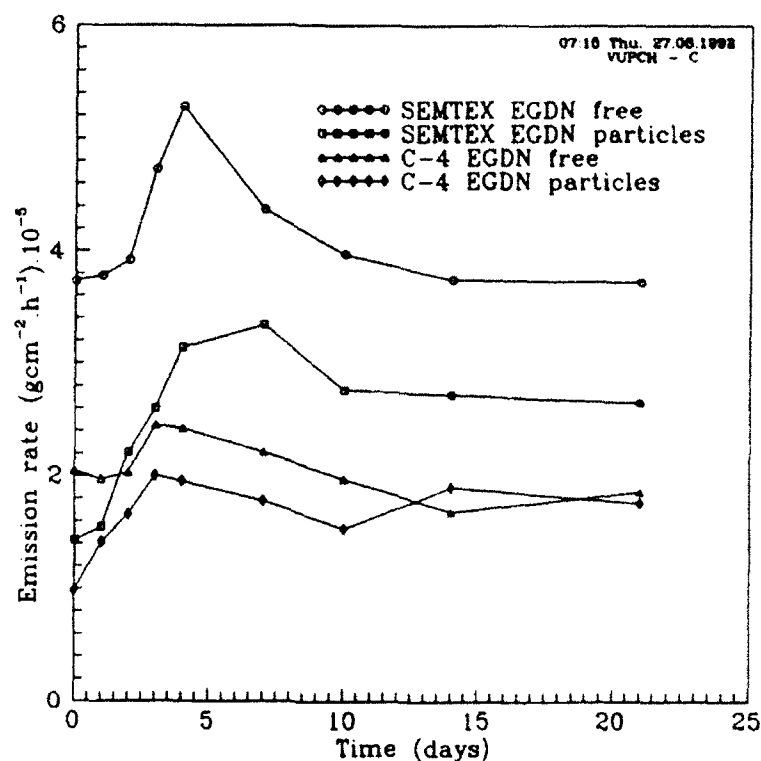


Figure 3. Change in emission rate of EGDN in time from C-4 and SEMTEX 1A

The results indicate that the composition and physical properties of plastic explosive have noticeable effect on the emission rate of EGDN. The estimated emission rate from C-4 was lower in comparison to SEMTEX. This fact is in contradiction with the higher concentration of marking agent in the binder of C-4 and the less closed surface of this explosive. It means, that some other aspects are important for the rate of emission of the marking agent. The chemical affinity of components forming binder to marking agent or physical - chemical properties of the surface of crystalline high explosive could affect the emission rate of EGDN. The emission rate of EGDN from SEMTEX is by approx 100 % higher than the respective value for C-4, the maximum emission rate is achieved in 3 - 5 days. When we take into account all factors which influence and decrease the emission and spreading of marking agent vapours from the explosive such a difference in emission rate is probably not very important.

6. Some remarks to the possible mechanism controlling the emission rate

Generally, at least 3 factors can control the emission of taggants from the explosive: the vapour pressure, the diffusion and the combination of both. To get some more information of the process of emission, the emission rate of EGDN and DMNB from SEMTEX 1A was studied using two different velocities of the air stream. The flow of the air stream in the sampling apparatus was 50 and 100 mlmin⁻¹ which corresponds to the velocities of 13.9 mms⁻¹ and 27.8 mms⁻¹ respectively over the surface of the explosive. The marking additives in the concentration of 0.2 % EGDN and 0.1 %

DMNB were used. The mass of the explosive sample was 10 g, the experiment being performed at 20 °C. The results obtained are presented in Figure 3.

The decrease in EGDN emission rate corresponds to the lower vapour pressure caused by the insufficient flow of EGDN from the explosive to the surface. This process is controlled by the diffusion rate of EGDN in the explosive. The course of curve 1 can be explained as follows: the horizontal short part represents the vapour pressure controlled emission, then insufficient diffusion of EGDN to the surface reduces the emission rate and after 7 hours the equilibrium is reached. Then the diffusion controlled emission takes place which is only 40 % of the value of the starting emission rate.

The lower emission of DMNB corresponds to lower vapour pressure and lower concentration of this compound in comparison to EGDN. The decrease of DMNB emission is small and the influence of the quantity of the air flowing over the surface of the explosive is important. The solid DMNB particles which are not dissolved but dispersed in the explosive can reach the full vapour pressure of this compound over the surface and therefore the vapour pressure is concentration independent.

The influence of the diffusion in this case can rise in time because particles of DMNB situated in the surface layer of explosive will be exhausted after some time. This stage was not reached in the experiment as shown by the curves 3 and 4 and the process was evidently vapour pressure controlled.

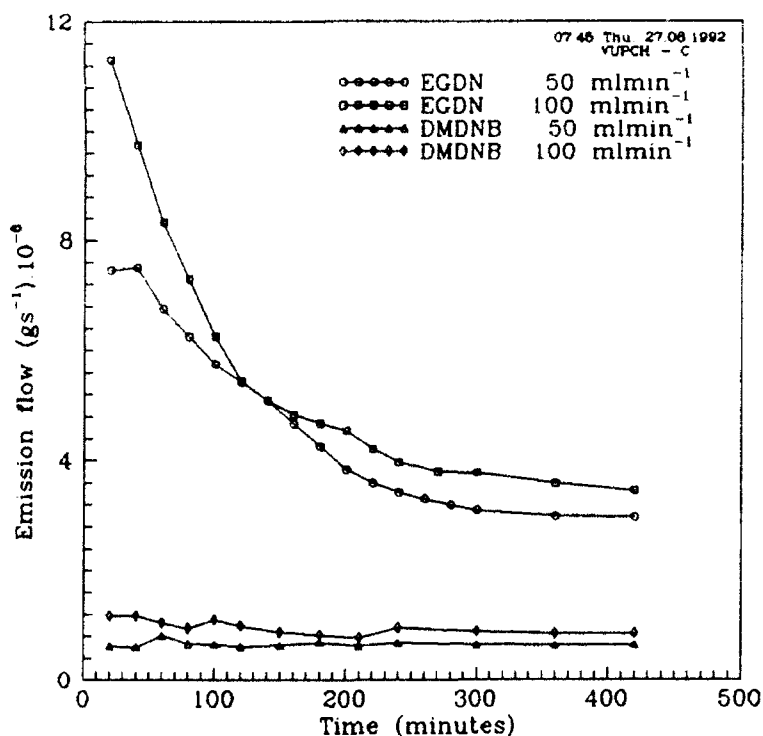


Figure 4. Emission rate of EGDN and DMNB at different air flow

7. Conclusion

- 7.1 A suitable method for measuring the emission rate of marking agents was developed.
- 7.2 The fluctuations of emission rate of EGDN from marked plastic explosive SEMTEX 1A produced in a plant scale are low, the mean value being $2.52 \cdot 10^{-5}$ ($\text{gcm}^{-2} \cdot \text{h}^{-1}$).
- 7.3 The maximum emission rate when marking particles are used is reached in several days, its value being approx. 150 % of that determined for a fresh explosive: this value is somewhat lower in comparison to free added EGDN.
- 7.4 The EGDN concentration dependence of the emission rate of EGDN from SEMTEX 1A is represented by a straight line in a range of 0.05 % - 0.2 %, a similar dependence was estimated at marked C-4.
- 7.5 The emission rate of marking agent is influenced by composition and physical-chemical properties of plastic explosive. However, these differences are not very important from the practical application point of view.
- 7.6 The emission rate of EGDN is controlled in conditions of air flow over the surface of explosive at the beginning by the vapour pressure, after some time the process is controlled by the diffusion of EGDN to the surface of explosive. The emission rate of DMNB is controlled for longer time only by the vapour pressure of DMNB.

ANALYSIS OF AIRFLOWS IN PERSONNEL SCREENING BOOTHS

JOHN R. HOBBS and EDWARD P. CONDE
Volpe National Transportation Systems Center
Research and Special Programs Administration
U. S. Department of Transportation
Kendall Square
Cambridge, MA 02142 USA

ABSTRACT. A finite element fluid dynamics software model, FIDAP 6.0, was used to model the air flow in two different personnel screening booth configurations; one a walk-in/walk-out booth and the other a walk-through booth. The various parameters modeled were streamline contours, speed contours, effects of puffers, and RDX concentration. For optimum results it is necessary to produce high velocity air flows and, in the case of the walk through booth, it is imperative to locate a high speed puffer on the side of the booth opposite the sampling ducts.

1. Introduction

During the past 10 years, several commercial personnel screening systems have been developed for detection of concealed explosives. Most of these systems are capable of detecting nitroglycerine and ethylene glycol dinitrate from dynamite. Some even have the ability to detect concealed TNT, but few have had success in reliably detecting vapors from plastic explosives. The problem is made even more difficult by the requirement that the sampling and detecting process be performed in very short periods of time, e.g., in 6 seconds as stipulated by the Federal Aviation Administration. This formidable problem consists of four steps: (1) sampling the air around a person; (2) capturing in some manner the explosives vapor; (3) transporting the collected vapor to a detection system; and (4) analyzing the collected vapor. To date, state-of-the-art detection limits have been achieved for most of the analytical techniques (step4), such as the gas chromatograph-electron capture detector, ion mobility spectrometer, chemiluminescent detector, and mass spectrometer. In the future, improvements in these techniques will most likely not be greater than an order of magnitude at

best. Therefore, any dramatic improvements in personnel screening systems must come from the other three steps listed above. Recently, there have been some developments in the step 2, trapping of explosives vapor, most notably the efforts of Sandia National Laboratory (silica surfaces), Ion Track Instruments (continuous rotary trap), and Thermedics, Inc. (coated metal surfaces). Step 3, transport of collected vapors, is one that cannot be controlled, except to adhere to the principle of doing as little to the sample as possible and keeping the transport distance as short as possible. A "magic" material for construction of sampling and transport lines has not been developed and efforts to date have directed us as to what materials do not make good sampling and transport lines. This leaves Step 1, the sampling of the air around the person, as the only other area for improvement. Only a limited amount of research effort has been devoted directly to this problem. An effort was undertaken to investigate the sampling characteristics of a prototype walk in/walk out screening system and a hypothetical walk through screening system using a new finite element fluid dynamics computer software called FIDAP 6.0.

2. Fluid Dynamics Software

The software was obtained from Fluid Dynamics International, Evanston, Illinois. The package uses the Finite Element Method (FEM) to simulate various types of fluid flow.

In FEM, the flow region is subdivided into many small regions, called finite elements. The partial differential equations describing the conservation of mass, linear momentum, and energy of the whole region are replaced by ordinary differential or algebraic equations for each element. An iterative solver is then selected for solution.

For a successful run the user must provide the following:

- (1) the cartesian points used to draw the flow boundary;
- (2) a finite element mesh within this boundary (see Figure 2);
- (3) input boundary conditions for velocity, pressure, temperature, chemical species;
- (4) the initial conditions;
- (5) description of all physical properties;
- (6) select an iterative solution method.

In the computer simulations described below, the effectiveness of the personnel screening systems is determined by how effectively RDX vapor is sampled and directed to the sampling inlet port. The RDX mass transfer coefficients used in these simulations were obtained from data presented by B. Kenna, et. al., [1].

The solutions obtained from the FEM allow one to visualize the flow streamlines in the booth and the speed, temperature, pressure, and species concentration contours. However, the solutions are steady state, and therefore, one cannot simulate an instantaneous release of a vapor species and follow the concentration in time.

3. Personnel Screening Systems

3.1. THERMEDICS WALK-IN/WALK-OUT BOOTH

A prototype explosives screening booth developed by Thermedtec for the Federal Aviation Administration is shown in Figure 1. The booth is designed so that the person enters the booth and walks to the front where he stands facing five sampling ducts, each in the shape of an exponential horn, positioned from the floor to just above the head. The front portion of the booth is a smoothed surface and, because of this, the booth has been described as an "open clamshell", a description that will be used in this paper. There are also provisions in the booth for warming the person with heat lamps and ruffling his/her clothes with four sets of alternating, high velocity puffers, two directed at the person's front and two directed at the person's back. The outlet flow speed of the puffers is approximately 24 ft/sec. When the person stands at the sampling location, a large pump is activated and air is exhausted from the booth at 375 l/sec for approximately 10 seconds, so that 3,750 liters of air are exhausted into the sampling ducts for collection and subsequent analysis. This system has detected vapors from plastic explosives concealed under a layer of clothing.

3.2 WALK-THROUGH BOOTH

There is also considerable interest in walk-through booths, as these would appear to be more desirable in high volume situations, such as airport security systems. In this configuration, the person enters the walk-through tunnel and stops at the sampling location, where there are sampling ducts on one side of the person and there may or may not be puffers on the other side of the person. Again, there is a sampling pump exhausting air from the booth through the sampling ducts for collection and analysis. There are very little details available describing the design of this type of booth and we

have chosen to assume booth dimensions, entrance velocities, and flow rates similar to those used in the Thermedtec clamshell booth described above.

4. Discussion of Results

In all the contour plots that follow, the exit velocity at the sampling ducts, is adjusted to produce the entrance air velocity desired at the open portions of the booth. In the RDX concentration plots, the emission rate of RDX was determined by the flow rate in the booth, and the emission rates were 0.02 picograms/cm²/sec at a flow of 2 ft/sec, 0.09 picograms/cm²/sec at a flow rate of 6 ft/sec, and 0.12 picograms/cm²/sec at a flow rate of 8 ft/sec. In all the speed contour and concentration plots that follow, the darker the shading, the higher the speed and the concentration, respectively.

4.1 THERMEDICS CLAMSHELL BOOTH

The finite element grid for the Thermedics clamshell booth is shown in Figure 2. In order to produce smooth, regular contour plots, it is necessary to have a very evenly spaced finite element grid, such as that shown in Figure 2. It represents a two-dimensional top view of the booth, with the person's body represented by the ellipse in the center of the booth, approximately 9 in from the front inlet ducts. The location of the RDX on the person is the rear, left-hand position, approximating the left rear pocket.

Figure 3 shows the streamline plot for the booth with an entrance velocity of 6 ft/sec and no puffers. Notice, that directly in front of the person there are areas of stagnation or dead volume from which no vapor would be sampled by the air flow in the booth. The speed contour plot for this situation is shown in Figure 4, and the fastest speed is at the inlet to the sampling duct, while there are areas of lower speed directly in front and behind the person. The RDX concentration plot for this case is shown in Figure 5, and it can be seen that a high concentration of RDX is hitting the wall of the booth. The effect of adding puffers to the booth is illustrated in Figure 6, which shows the streamline plot for four 75 ft/sec puffers directed at the person. Notice that the eddies in front of the person have disappeared. The speed contour plot is shown in Figure 7, and it can be seen that the velocity around the edge of the person is higher with the puffers. The most notable difference in using the puffers is that a lower concentration of RDX is hitting the walls of the booth, as shown in Figure 8.

The effect of varying the flow or the sampling rate of the collection system is shown in Figures 9, 10, and 11. The location of the RDX is on the left front of the person and only one-half of the booth is shown. The RDX contour plots are presented for 2, 6, and 8 ft/sec flows, respectively. At the lower flow rate, a higher concentration of RDX is hitting the walls than at the higher flow rates. Clearly a high flow rate is desirable.

The effect of varying the position of the person is illustrated in Figures 12 and 13 for an entrance velocity of 8 ft/sec for positions closer to and further away from the sampling duct, respectively. It can be seen that at the same flow rate a higher concentration of RDX is hitting the walls, the further the person is from the sampling ducts. Therefore, the closer the sampling duct is to the person, the higher the RDX concentration that is sampled and the lower the RDX losses to the walls of the booth.

Another variable would be to move the walls of the booth as close to the person as possible, making the streamlines closer together and increasing the velocity around the person. Unfortunately, nothing is gained in doing this, as illustrated in Figure 14 for an entrance velocity of 2 ft/sec, compared with the RDX concentration plot of Figure 9 for the normal booth and entrance velocity of 2 ft/sec. If the walls are moved closer to the person, the situation can be improved by increasing the entrance velocity, as illustrated by the RDX concentration plot shown in Figure 15 for a booth with narrow walls and an entrance velocity of 8 ft/sec. Even at the higher flow rate, it can be seen by comparing Figures 11 and 15 that the closer the wall is to the person, the more RDX will hit the wall of the booth and be lost.

The results of this analysis indicate that, for the clamshell booth, high speed puffers help the sampling of RDX, that the sampling duct should be as close as possible to the person being sampled, and that as high a sampling flow rate as possible, commensurate with the sample collection system, should be used in the booth.

4.2 WALK-THROUGH BOOTH

The finite element grid for the walk-through booth is shown in Figure 16. Figure 17 shows the speed contour plot for an entrance velocity of 6 ft/sec and no puffers. The velocity in front of the person is high, but the velocity at the sides is lower, and the velocity behind the person is a factor of almost 50 lower than in front of the person. This means that there is no flow behind the person and therefore, no chance of sampling explosives vapor

concealed there. The situation is improved somewhat when a 30 ft/sec puffer is added in the booth on the side opposite the sampling ducts, as shown in the speed contour plot of Figure 18. Now there is increased velocity on the side of the person opposite the sampling ducts, and the chance of sampling RDX has improved considerably. However, there remains a large area near the back of the booth, where there is still very little flow, and if RDX vapor were captured in this area it would not be detected. Dramatic improvements are obtained if the puffer velocity is increased to 60 ft/sec as shown in Figure 19. Now flow is seen in almost all regions at the back of the booth and there is high velocity all around the person. We would expect increased performance if the puffer velocity were increased further.

Finally, in the last set of Figures we see the effect of the puffers on the RDX concentration contours. In Figure 20 we see that with no puffer at the back of the booth, a considerable amount of RDX vapor transports to the back wall and is lost. The addition of a 30 ft/sec puffer, as shown in Figure 21, reduces the losses to the back wall by around an order of magnitude. Increasing the puffer velocity to 60 ft/sec effectively keeps all the RDX off the back wall, as illustrated in the RDX concentration plot of Figure 22.

For any type of walk through booth, the results of this analysis clearly show that it is imperative that there be a velocity of air 60 ft/sec or greater blowing on the person from the side of the booth opposite the sampling ducts. This puffer velocity is tied to the entrance air velocity, which in this simulation was 6 ft/sec.

5. Acknowledgement

This work was sponsored by the Security Research and Development Service of the Federal Aviation Administration Technical Center.

6. Reference

- [1] Kenna, B., Conrad, F. J., and Hannum, D.W. (1992) 'Explosive Vapor Emission', Proceeding of the First International Symposium on Explosive Detection Technology, FAA Technical Center, Atlantic City, N.J., pp 510-517.

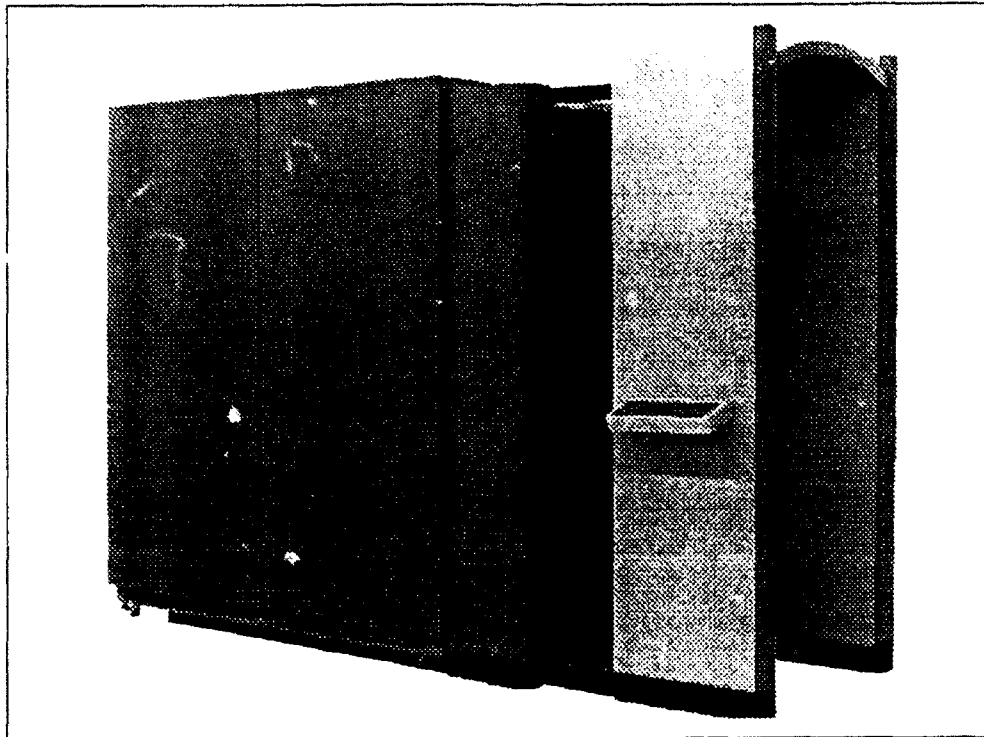


Figure 1. Thermedics Prototype Clamshell Personnel Screening Booth.

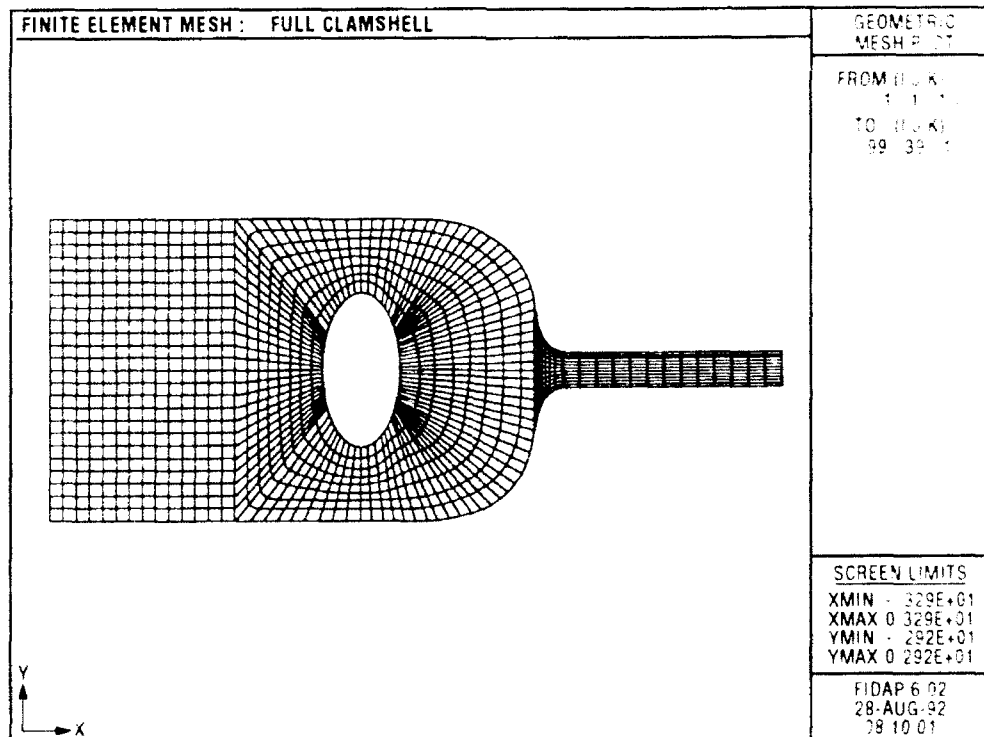


Figure 2. Finite Element Grid for Clamshell Booth.

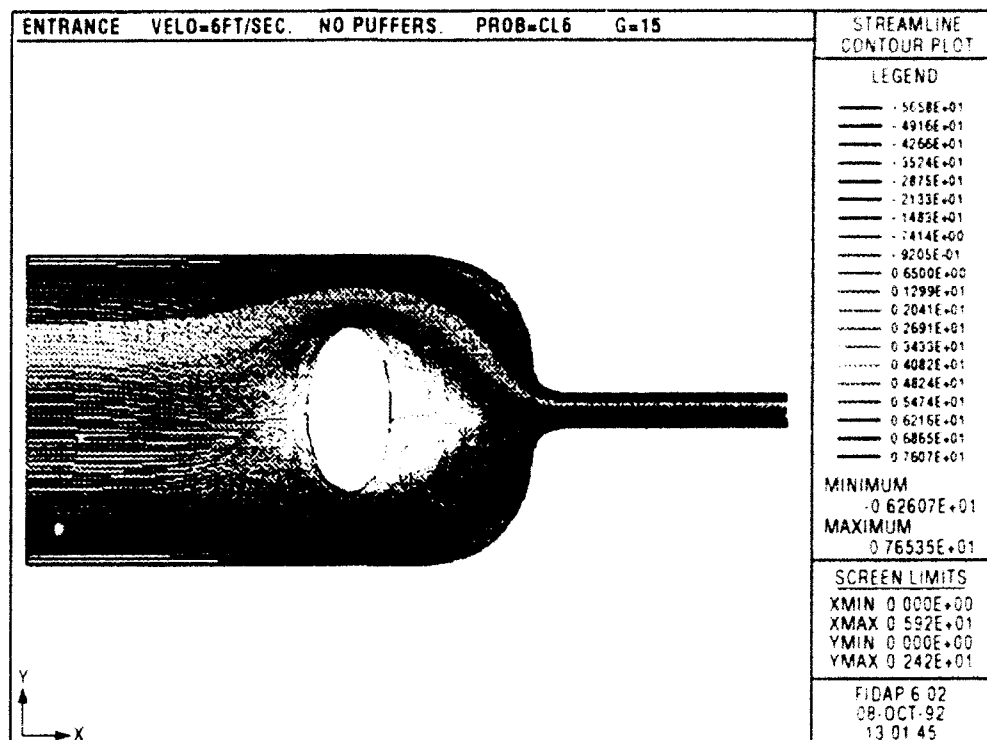


Figure 3. Streamline Plot for Clamshell Booth with Entrance Velocity 6 Ft/Sec.

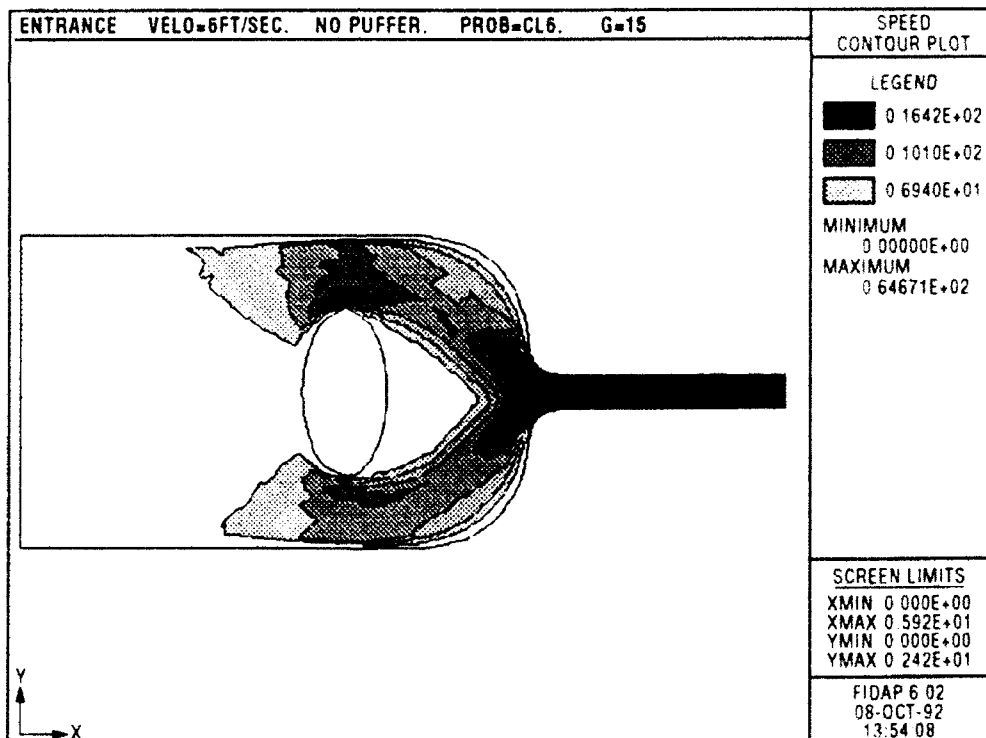


Figure 4. Speed Contour Plot for Clamshell Booth with Entrance Velocity 6 Ft/Sec.

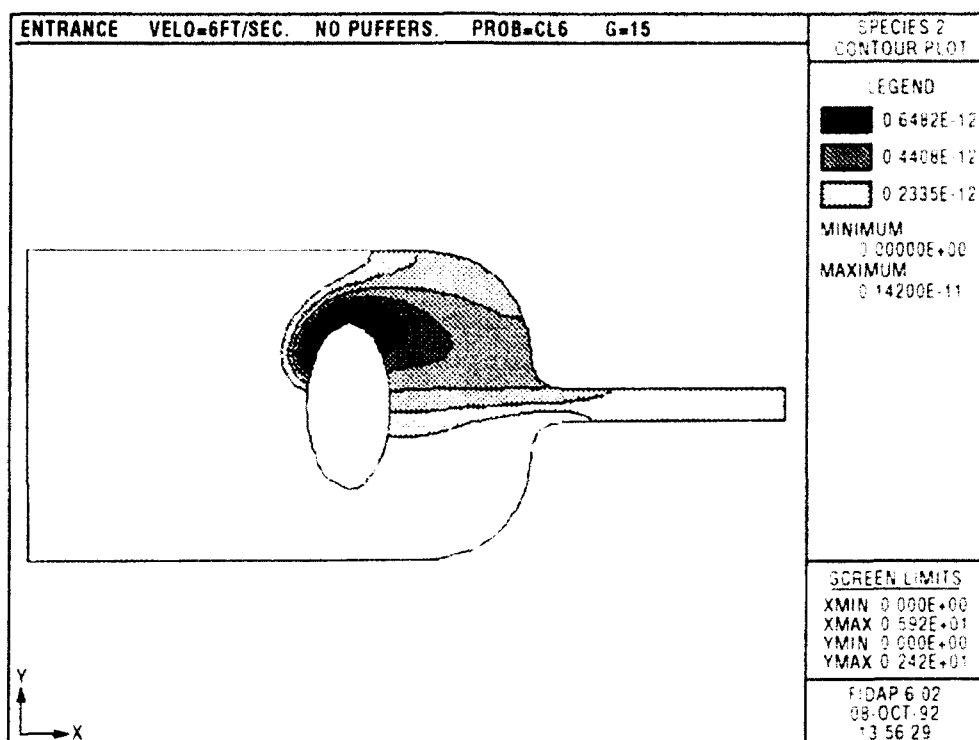


Figure 5. RDX Concentration Plot for Clamshell Booth with Entrance Velocity 6 Ft/Sec.

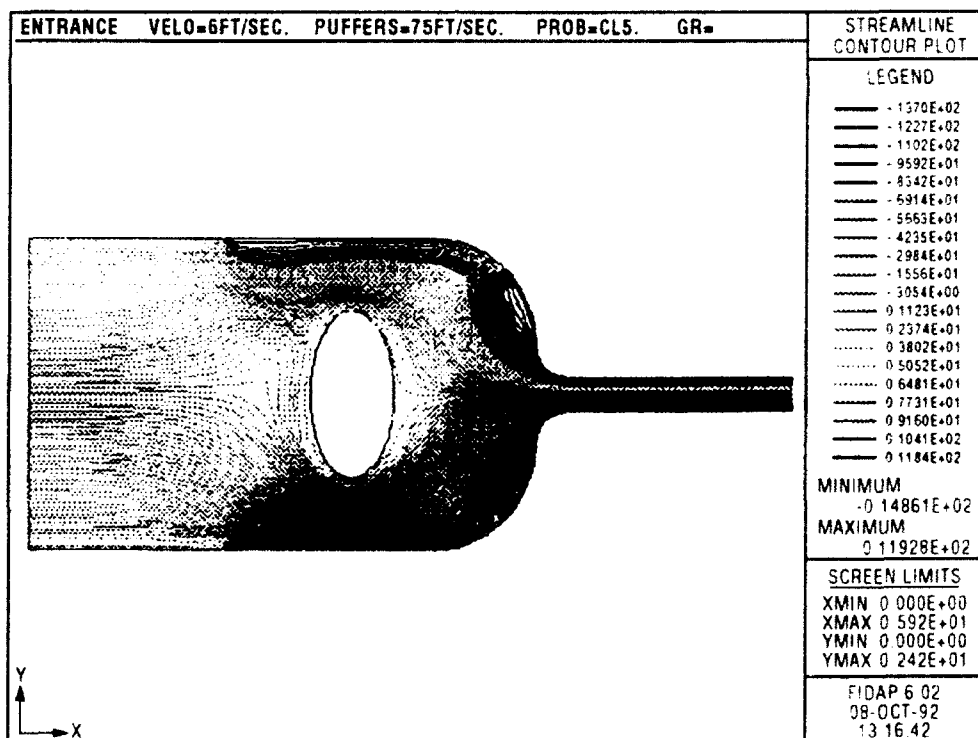


Figure 6. Streamline Plot for Clamshell Booth with Entrance Velocity 6 Ft/Sec and Puffer Velocity 75 Ft/Sec.

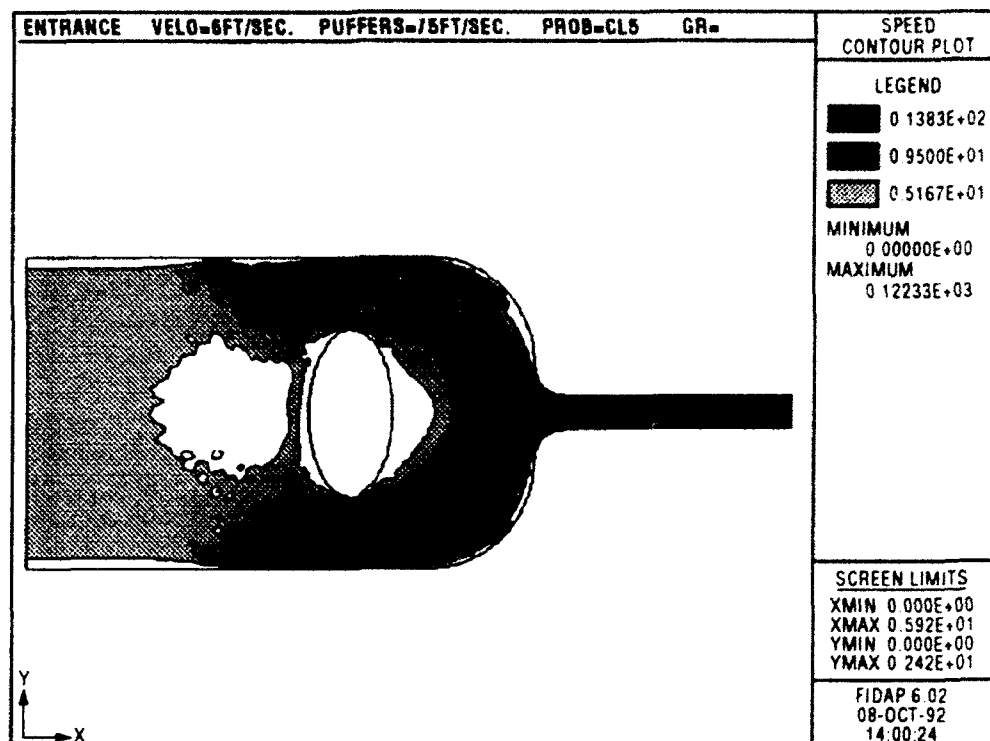


Figure 7. Speed Contour Plot for Clamshell Booth with Entrance Velocity 6 Ft/Sec and Puffer Velocity 75Ft/Sec.

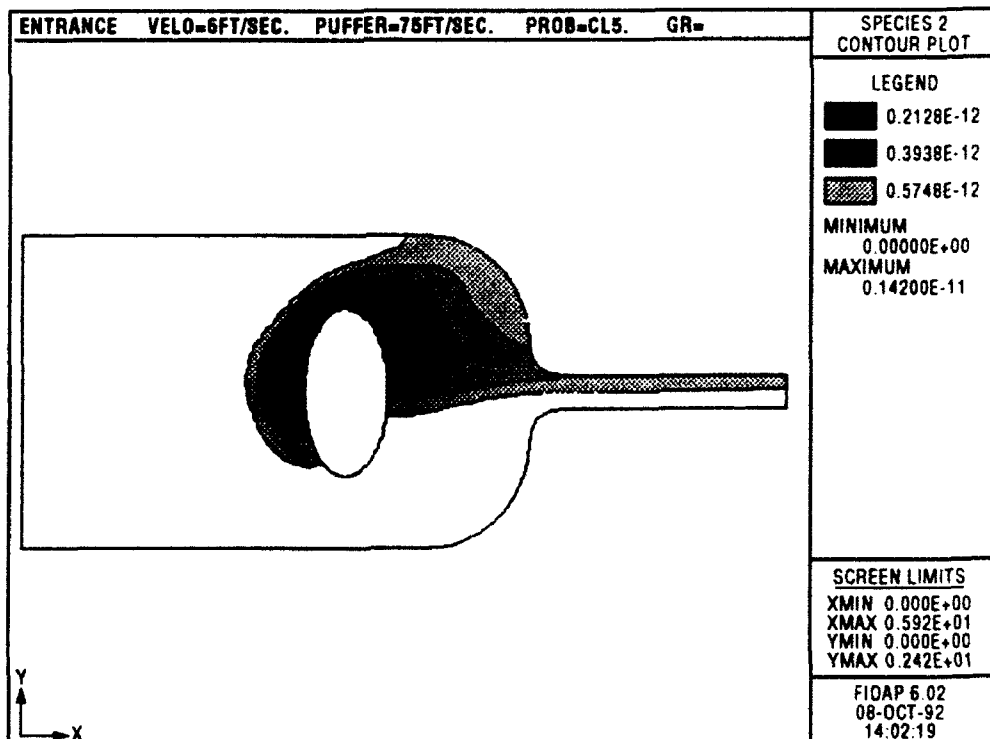


Figure 8. RDX Concentration Plot for Clamshell Booth with Entrance Velocity 6 Ft/Sec and Puffer Velocity 75 Ft/Sec.

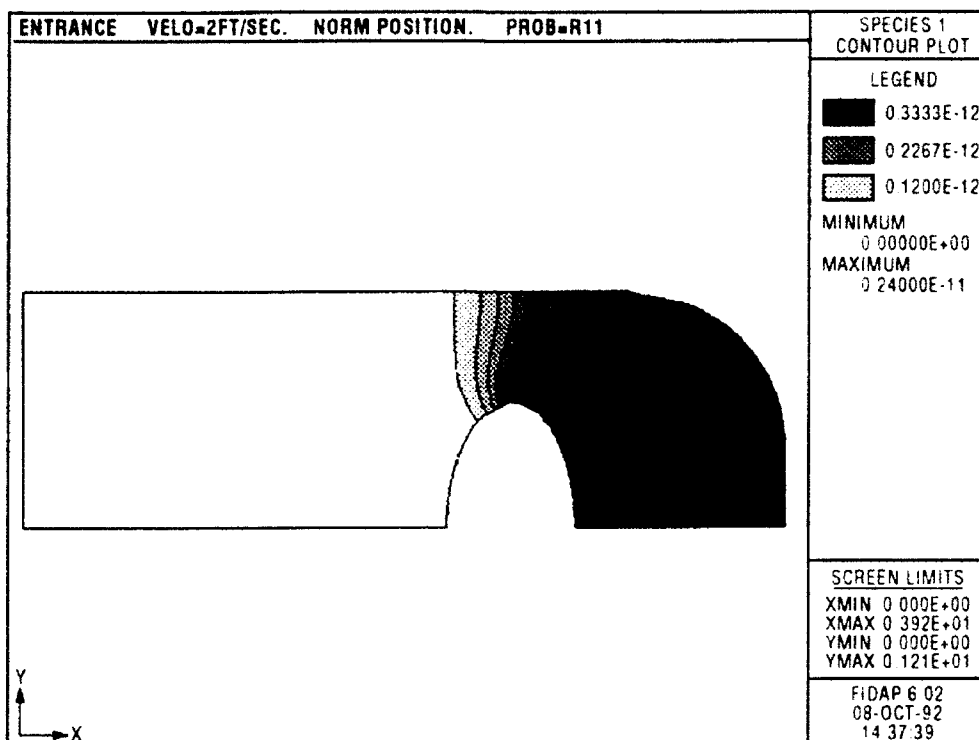


Figure 9. RDX Concentration Plot for Clamshell Booth with Entrance Velocity 6 Ft/Sec for Normal Body Position.

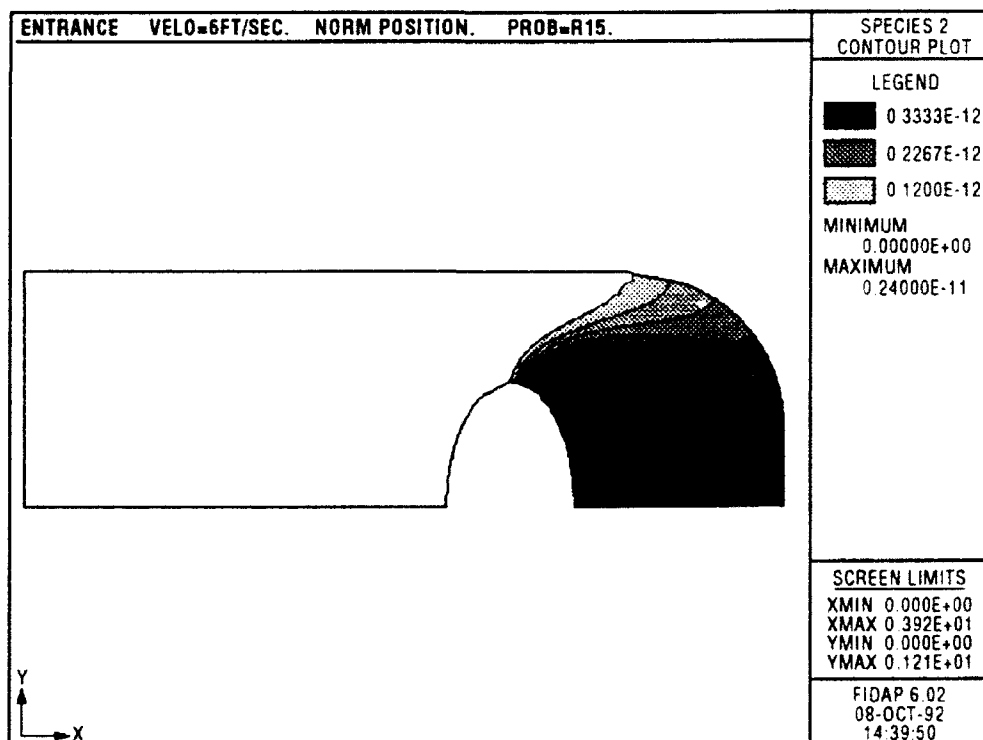


Figure 10. RDX Concentration Plot for Clamshell Booth with Entrance Velocity 6 Ft/Sec for Normal Body Position.

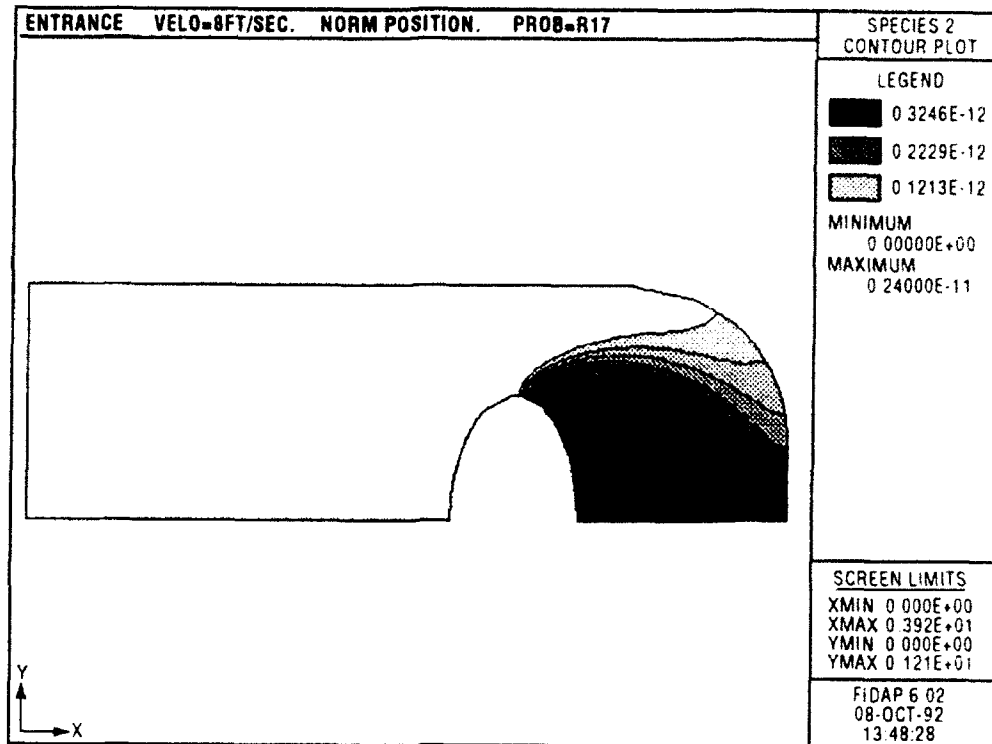


Figure 11. RDX Concentration Plot for Clamshell Booth with Entrance Velocity 6 Ft/Sec for Normal Body Position.

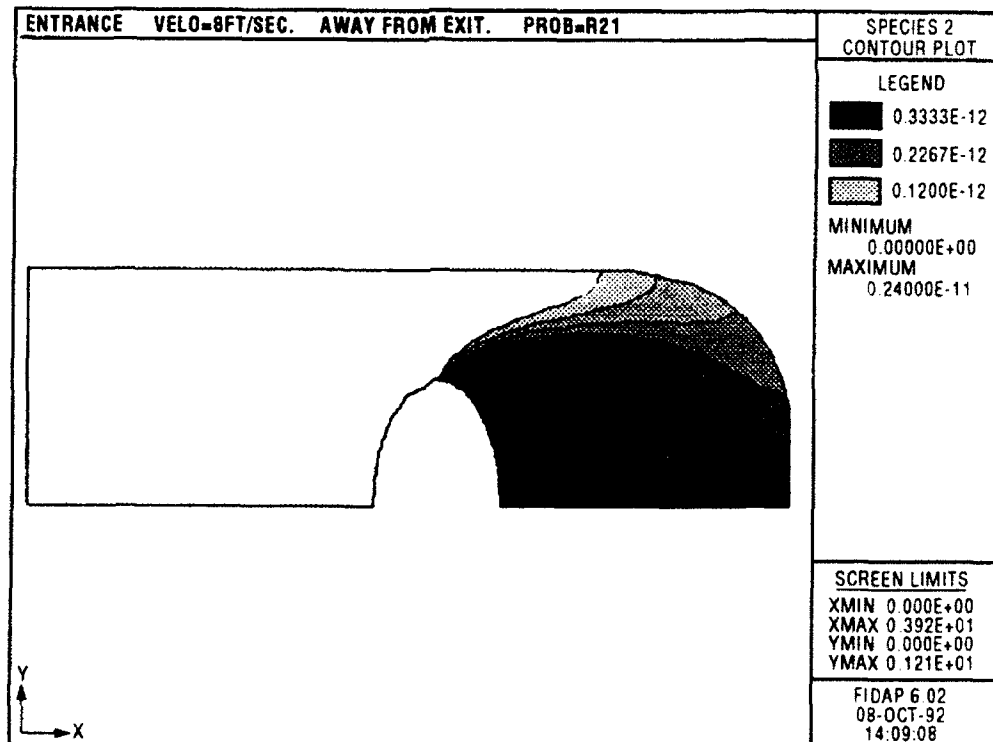


Figure 12. RDX Concentration Plot for Clamshell Booth with Entrance Velocity 8 Ft/Sec for Away Body Position.

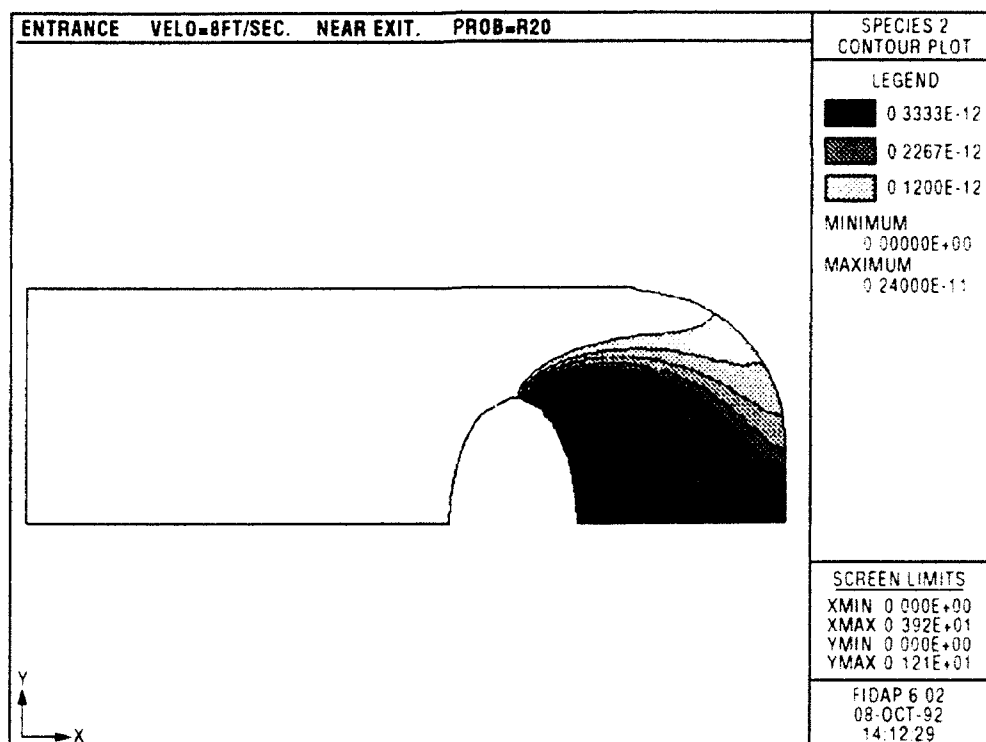


Figure 13. RDX Concentration Plot for Clamshell Booth with Entrance Velocity 8 Ft/Sec for Near Body Position.

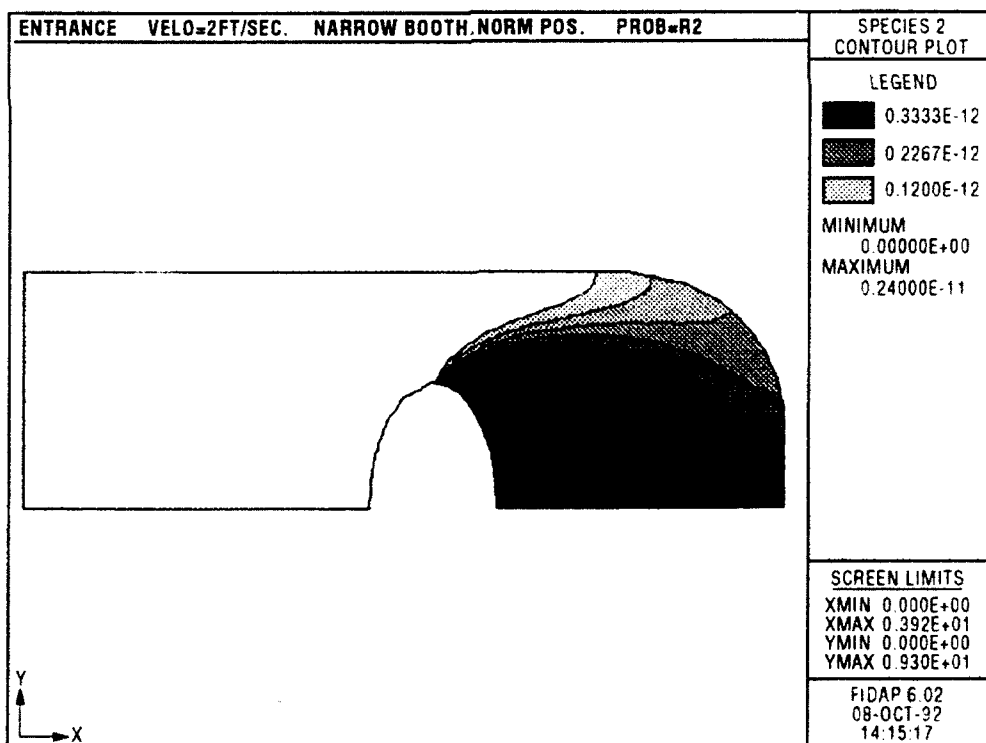


Figure 14. RDX Concentration Plot for Narrow Clamshell Booth with Entrance Velocity 2 Ft/Sec for Normal Body Position.

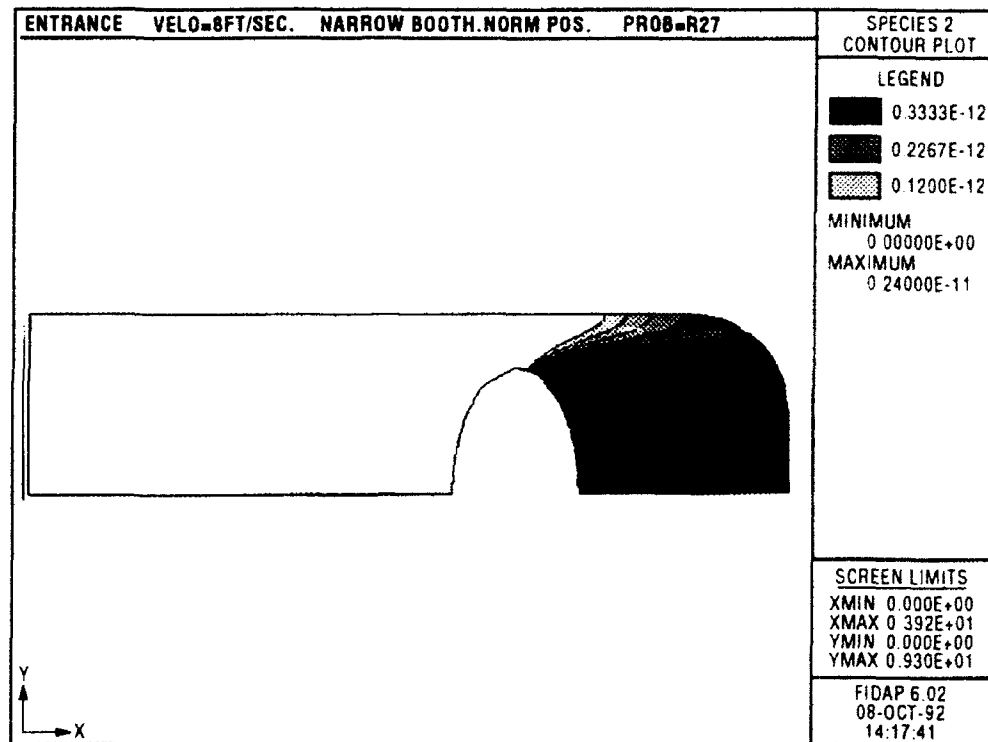


Figure 15. RDX Concentration Plot for Narrow Clamshell Booth with Entrance Velocity 8 Ft/Sec for Normal Body Position.

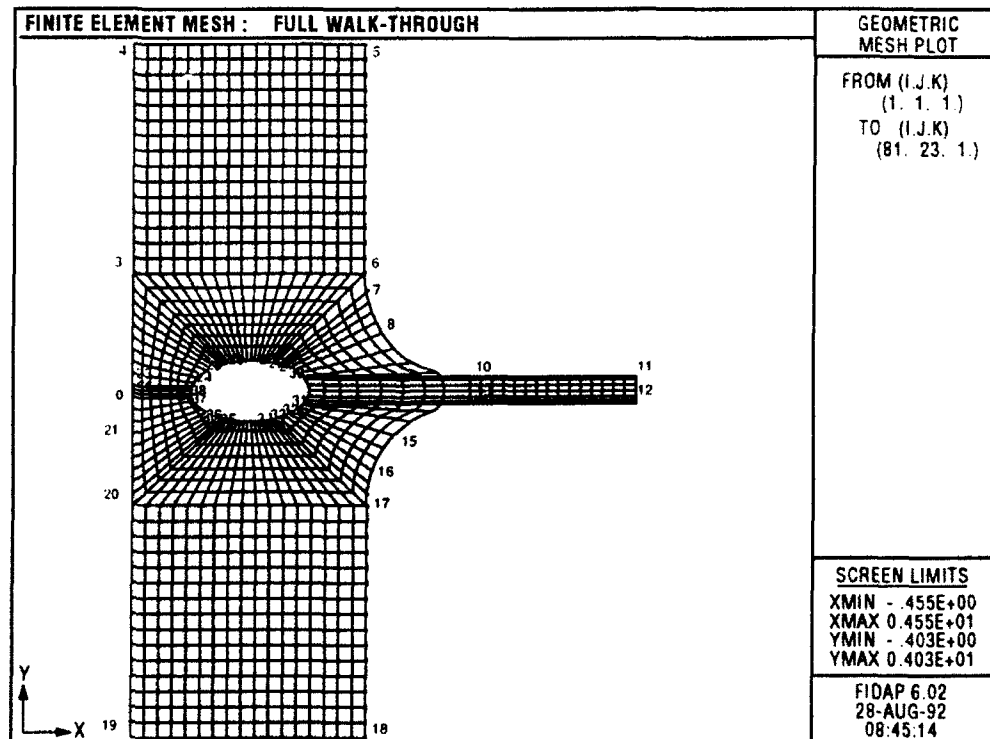


Figure 16. Finite Element Grid for Walkthrough Booth.

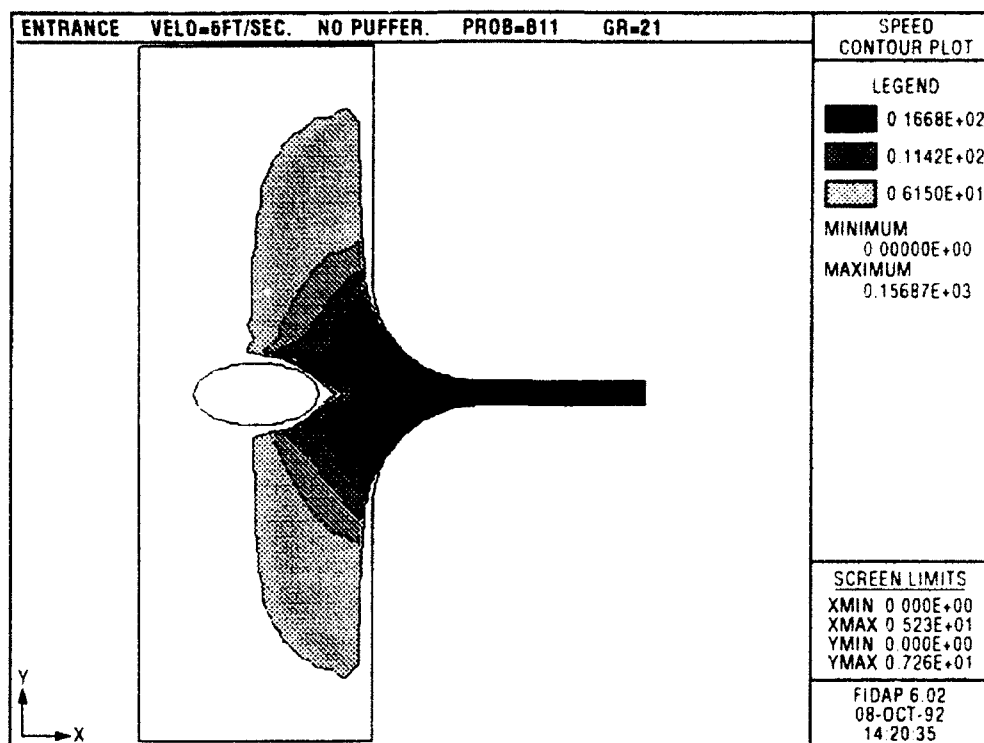


Figure 17. Speed Contour Plot for Walkthrough Booth with Entrance Velocity 6 Ft/Sec No Puffers.

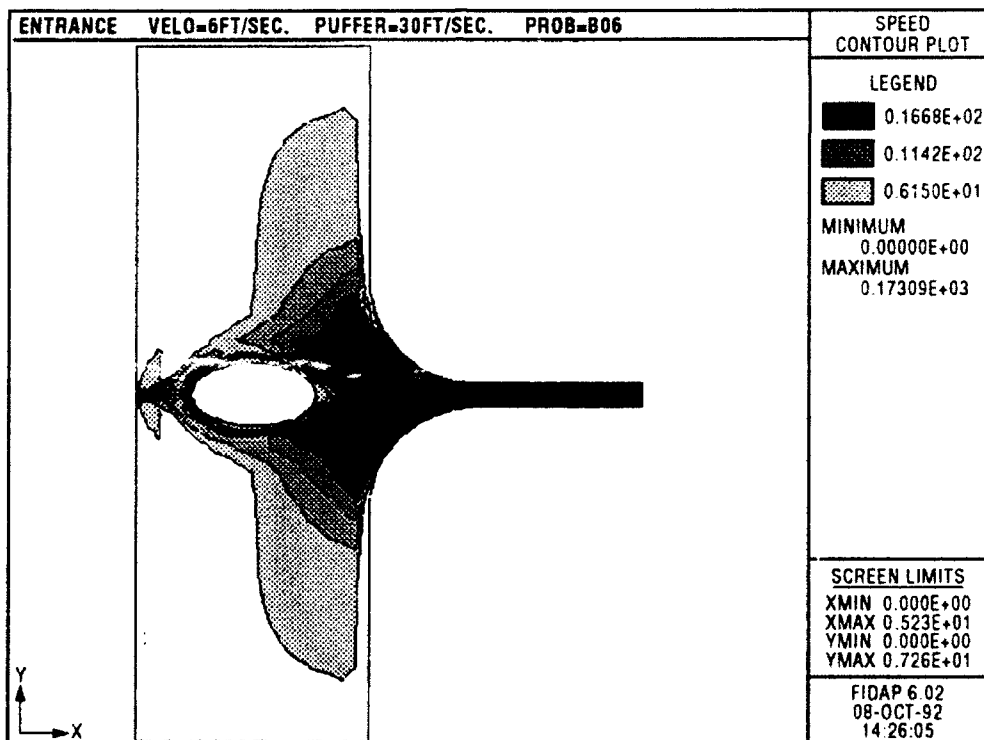


Figure 18. Speed Contour Plot for Walkthrough Booth with Entrance Velocity 6 Ft/Sec and Rear Puffer Velocity 30 Ft/Sec.

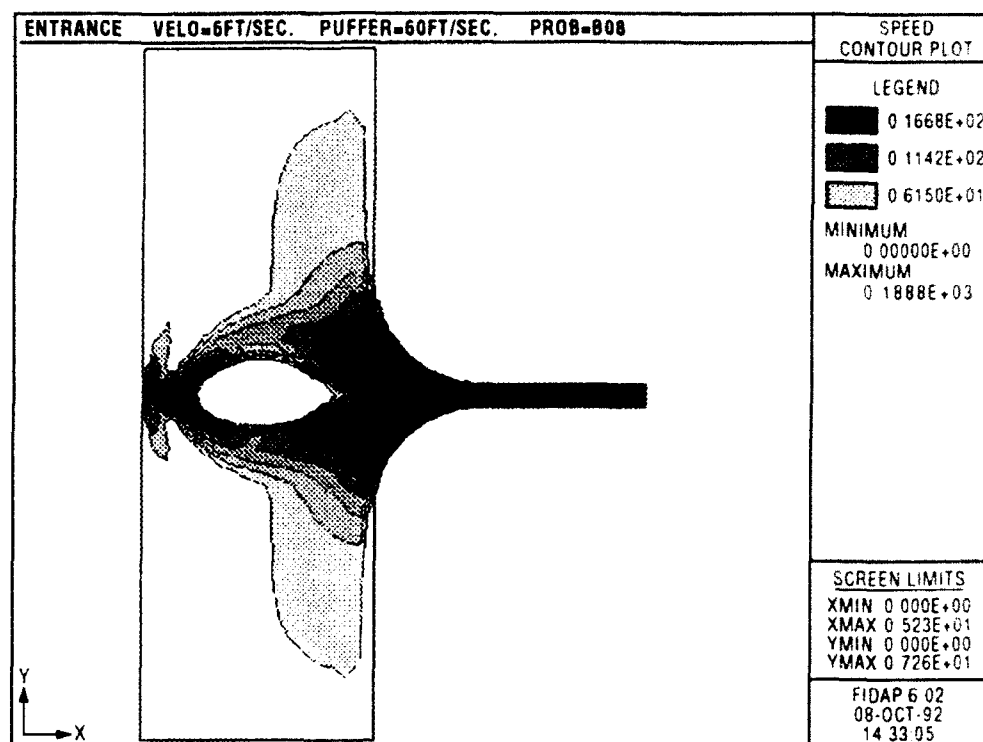


Figure 19. Speed Contour Plot for Walkthrough Booth with Entrance Velocity 6 Ft/Sec and Rear Puffer Velocity 60 Ft/Sec.

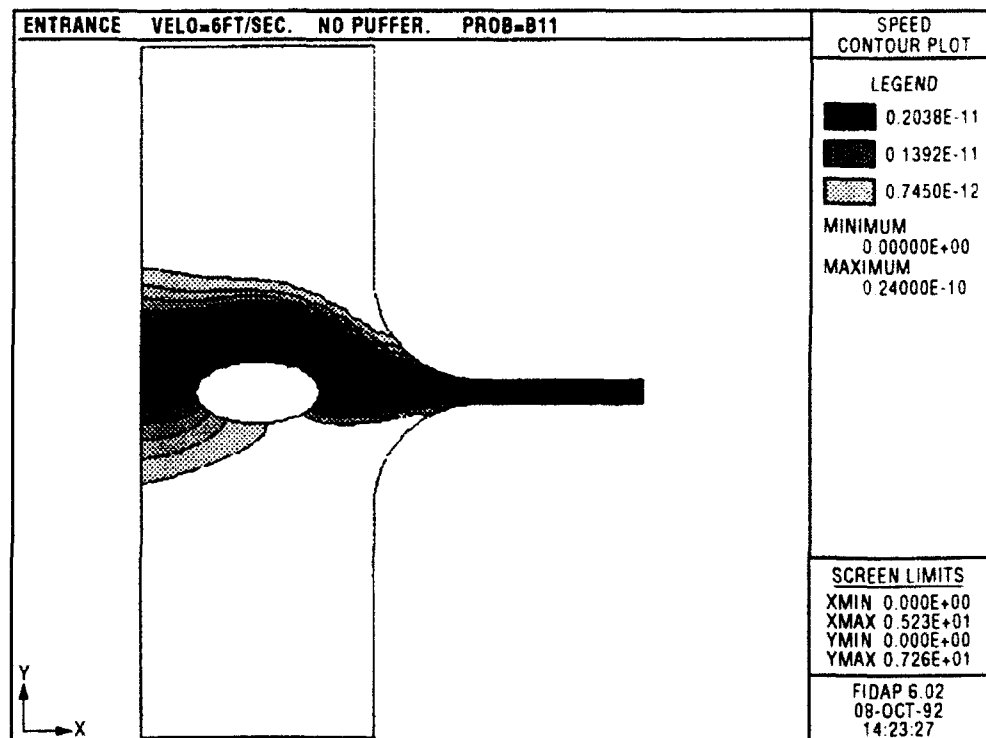


Figure 20. RDX Concentration Plot for Walkthrough Booth with Entrance Velocity 6 Ft/Sec and No Rear Puffer.

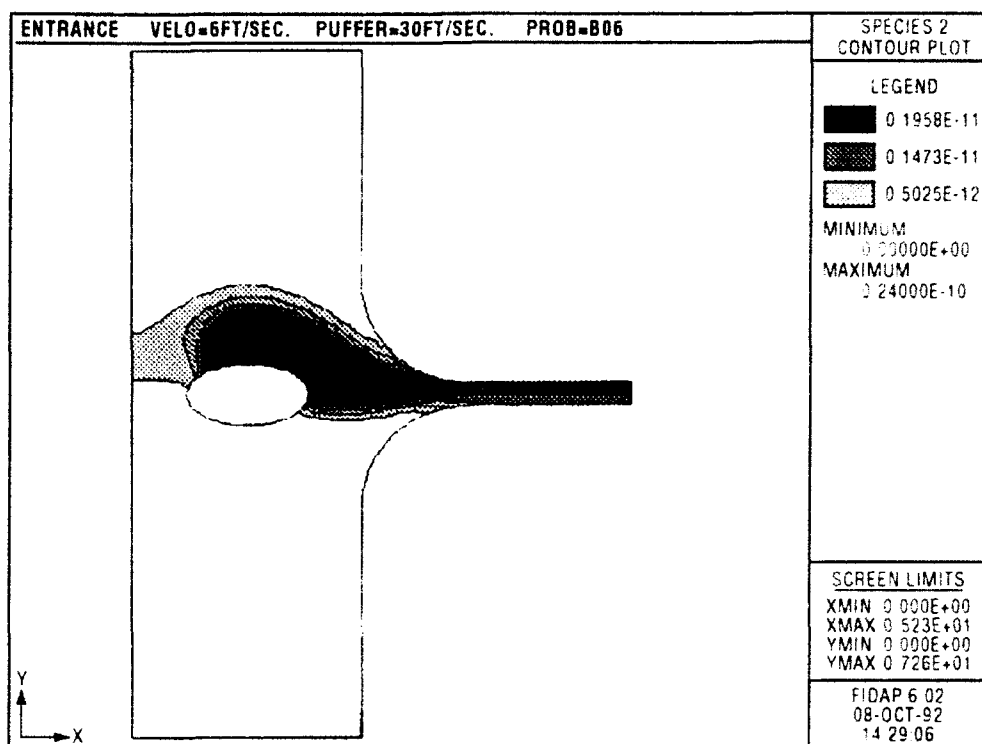


Figure 21. RDX Concentration Plot for Walkthrough Booth with Entrance Velocity 6 Ft/Sec and Rear Puffer Velocity 30 Ft/Sec.

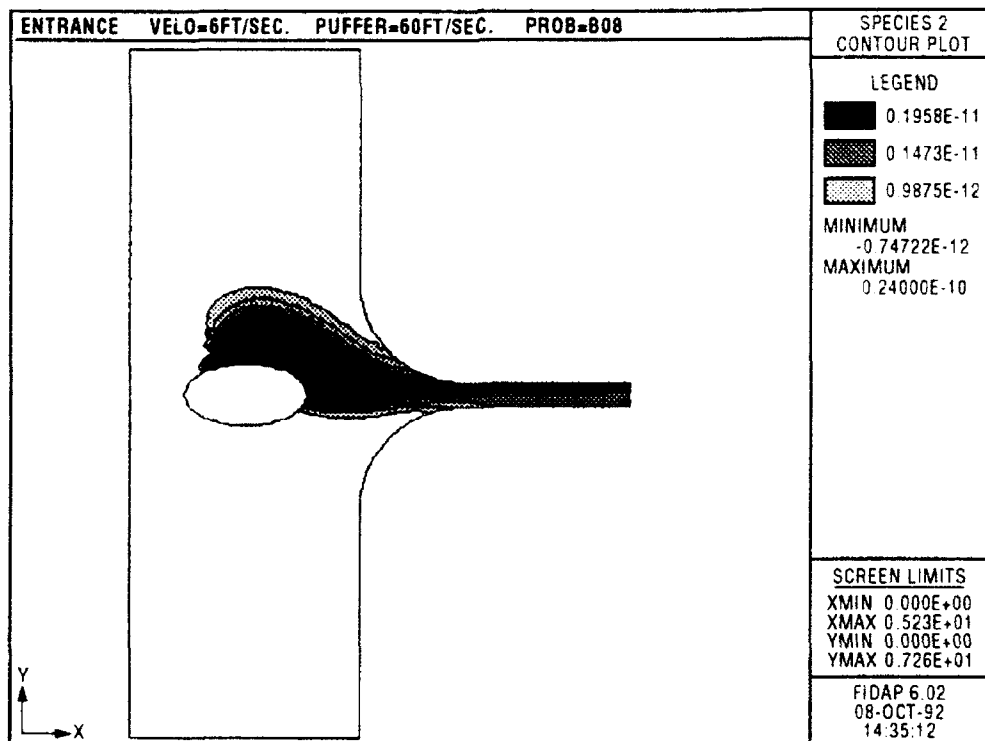


Figure 22. RDX Concentration Plot for Walkthrough Booth with Entrance Velocity 6 Ft/Sec and Rear Puffer Velocity 60 Ft/Sec.

THE ATF CANINE EXPLOSIVES DETECTION PROGRAM

RICHARD A. STROBEL, ROBERT NOLL AND CHARLES R. MIDKIFF JR.

Bureau of Alcohol, Tobacco and Firearms

Forensic Science Laboratory

1401 Research Blvd.

Rockville, Maryland, United States 20850

ABSTRACT: Explosives detection technology has advanced significantly in the past few years. Even with those advances many of the instrumental techniques still are unable to meet current needs. Additionally, evaluation of several canine explosives detection programs found them to be deficient on an operational basis. In response, ATF developed a pilot training program for explosives detection canines in 1991. The training concepts used included: 1. food reward conditioning; 2. scientific oversight of proficiency testing; 3. use of small amounts of a wide range of explosive compounds representative of those in use today. Advantages of the training program included dogs capable of working with multiple handlers and sensitive to a wide range of concealed explosive products at quantities as low as 15 grams. Additionally the training program could be completed in six weeks and at minimal cost.

Introduction

Since the initial work at the Army Land Warfare Laboratory in 1971 [1] and other early studies [2,3], dogs have been used for detection of bombs and explosives. In 1990 ATF began a joint program with the U.S. Department of State and the Connecticut State Police to produce a more effective explosives detection canine (K9). Prior to this time, our experience with canine explosives detection had been mixed. We had encountered both excellent programs and programs which were operationally unsound. It was our belief that the experience gained in our accelerant detection K9 program could be used to build an improved program for canine explosives detection. Our objective was to develop search dogs capable of detecting a greater variety of explosives than those trained under existing programs. In addition, greater flexibility in operational use of the dogs was desired. We were familiar with programs used to train dogs to detect drugs, weapons and explosives [4-5] and with the limitations of the instrument based technology for explosive detection. Clearly, trained canines could, in some instances, more effectively fulfill many of the missions assigned to machines and do so at lower cost. A major advantage of dogs is their mobility, a significant improvement over fixed detector installations, which need only be circumvented by a terrorist placing a bomb or smuggling explosives. In examining the canine programs which were operational today, several key areas were identified for improvement. These key areas provided the focus for our pilot program.

Pilot Program Goals

The pilot program identified three major goals. These were: 1) Systematic selection of explosives for training, 2) Standardization of testing and evaluation procedures and 3) Elimination of cross-contamination of explosive odors. In the programs examined, there appeared to be no identified system for the choice of the explosives the dogs were trained to detect. In one program, the dogs were trained to detect C-4 and TNT [4], neither of which appear to pose a major threat in the United States. In another, the dogs may have a knowledge of 14 different types of odors including drugs, human odors and explosives [5]. Most programs train on a variety of explosives products but often significant families of explosives are omitted. This may be due to either sample availability problems or a lack of knowledge of the chemical components of many explosives. For example, in one study utilizing dynamite, it was assumed that nitroglycerin was the primary olfactory stimulant relied upon by the dog for detection [6]. Only subsequently was it learned that in dynamite, ethyleneglycol dinitrate (EGDN) was the major component of the vapor, a fact well known at the time by users of vapor based explosive detection instruments. It is estimated that there are over 19,000 known explosives compositions worldwide, it is therefore impractical to condition a dog to each. Nevertheless, the vast majority of explosives are composed of a relatively small number of chemical compounds or ingredients. For example, whether the explosive is TOVEX, made by ETI of Canada, Atlas 7D, made by ICI, Austin Emulex, ANFO or any of several thousand commercial blasting or improvised explosive mixtures, the one common ingredient is ammonium nitrate. The same is true of most other widely used explosive compositions. To simplify matters, both high and low explosive compounds were categorized into chemical families for the purpose of training.

Classification of Explosives for K9 Training

For training purposes, the explosives were classified as: Nitro Compounds, subdivided into aliphatic and aromatic, Nitrate esters, Nitramines, and acid salts. Pure samples of the major explosive compounds in each chemical family were obtained for training the dog. Many were obtained in pure form from a commercial product, for example, PETN from the core of commercial detonating cord. Some were purchased as the chemically pure reagent, e.g. Ammonium Nitrate, Potassium Perchlorate, etc. By training the dog with the pure explosive, the dog will recognize any formulation containing that particular component. Therefore, rather than training the animal on an explosive of specific composition such as C-4, Semtex, U.S. Military dynamite, British PE-4 or other similar material, a dog trained to alert on RDX should alert on any formulation containing it. A significant advantage of this approach is the ability of the dog to recognize improvised formulations. With PETN, for example, some terrorists groups are known to plasticize the PETN using their own formulation. A dog trained to recognize the pure explosive should detect a PETN containing explosive regardless of the matrix. **SEE APPENDIX I**

The Training Program

ODOR RECOGNITION CONDITIONING WITH THE SCENT BOX

The training methodology used to condition the dog to a specific explosive odor relies initially on the use of a scent box. A small quantity, about 3 grams, of the explosive is placed in a tin box perforated with 6 holes approximately 5 millimeters in diameter. The box serves both to focus the dog on an object and to protect against accidental ingestion. Conditioning proceeds with the dog obtaining a reward of food upon inhaling/exhaling at the surface of the box. The training exercise is repeated until the dog always responds to the odor, at which time the dog is considered conditioned.

USE OF THE FOOD REWARD FOR TRAINING

A food reward conditioning method was chosen over several alternative methods because it offered advantages in speed of training, a stronger stimulus and the potential for the use of multiple handlers. The length of the training period is both an operational and an economic consideration and a food reward approach has distinct advantages in this area. During the conditioning phase of training, the dog can be subjected to many repetitions in the course of a work day by metering out small portions of food as the exercise proceeds, never allowing the dog to become completely full. This would be difficult with other reward systems such as those relying on praise or play. Food provides a strong stimulus for performance; the dog is never fed without exposure to an explosive scent. They are literally trained to "think" that they must smell an explosive in order to eat. A conditioned stimulus based upon a survival instinct is a very strong motivator.

The food reward also offers the potential for use of multiple handlers; the dog will work with anyone who will feed it. This is a distinct advantage over the widely used "bonded team" because the dog can work effectively with an alternate trained handler when the normal handler is unavailable. The ability to use alternate handlers lends much greater versatility to an otherwise highly specialized canine detection system.

THE TRAINING WHEEL

After initial conditioning another training aid, the training wheel, is utilized. The device consists of four containers on a rotating wheel. One can is the "hot" or positive sample container and the remainder contain either no samples or samples with distracting odors ("distractors"). With this device, the dog can be worked "off-lead" on a continuing basis until the correct response is obtained. At this point, the dog has been conditioned to first smell explosives and then receive a food reward. Conditioning is considered successful when the dog ignores a food distractor in favor of the explosive odor stimulus. The dog has been conditioned to only eat after detecting explosives. Integral to the training program are other skills such as basic obedience, search techniques and a correct non-aggressive response when alerting to explosives. Familiarization of the handler with search techniques and effective use of the dog is an essential part of the training program.

TESTING AND EVALUATION

Previous procedures for testing and evaluating the performance of canine teams have frequently been poorly designed and lacked scientific oversight. For the testing in this pilot project, a set of scientific protocols was established to objectively evaluate performance and remove the sources of criticisms of prior programs. Sample handling and preparation procedures were designed and conducted in a manner to avoid cross-contamination between explosives and between explosives and negative or blank cans. Care is also taken to avoid the introduction of other scents, such as those of the handler, which may "que" the dog to a particular sample.

Results

To date, a pilot project consisting of four dogs and four handlers has been completed in a 6 week period ending in September 1991. This represents a significant improvement over a reported training time of two months or more [5] or 12 weeks for drug detecting dogs [7]. The dogs in the pilot project were trained using food reward conditioning on three gram quantities of eight explosives. The explosives used were selected to cover a wide range of products currently in use worldwide and to provide a representative sample from each of the explosive families previously described. Wherever possible, products containing the pure explosive compounds were used. Evaluation at the end of the 6 week training period consisted of a blind test using 15 gram quantities of 20 different explosive products. Each of these products contained one or a combination of the original explosives on which the dogs were conditioned. The explosives were placed in scent boxes which were then placed in one quart open metal cans. The purpose of the cans was to provide a known, uniform volume of dead air space above the scent box to allow the dogs equal access to the odor. This helps to nullify differences due to changing sample environment, air currents, etc. Empty scent boxes in one quart cans were used as negative or control samples. All four dogs were able to identify all 20 explosives. Additional operational testing, such as room, vehicle and baggage searches were equally successful.

Contamination of the training explosives by EGDN was a serious limitation of some prior studies. To avoid this in the pilot study, dynamite was not used in any of the training. However, the ability of the dogs to detect dynamite was demonstrated and confirmed during operational testing by secreting a small quantity of dynamite in a vehicle. Future studies will more closely monitor EGDN and other sources of potential cross-contamination problems.

Conclusion

The use of a systematic approach in selecting the explosives for initial conditioning reduces the number of explosive products to which the dog must be exposed for training. At the same time, systematic selection allows the dog to detect the widest possible range of explosives when working in the field, whether they are commercial products or improvised mixtures. This selection also allows the K9 explosives team to detect a wide variety of explosives not readily detectable by current explosives detection instruments.

The use of standardized protocols and testing procedures provides accurate and credible results and an objective assessment of the performance of the detection team. The training methodology

using food reward conditioning has been shown to be a rapid and effective means for canine training, producing a versatile, highly motivated and sensitive explosives detection system.

FUTURE OF THE PROGRAM

Beginning in October, 1992, ATF, in conjunction with the Connecticut State Police and the U. S. Department of State, is implementing a program which will provide 200 trained explosive detection canine teams for deployment worldwide. Through its Antiterrorism Assistance Program, the U.S. State Department will enter into agreements to provide dogs and training to selected governments to provide them with effective canine explosives detectors.

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APPENDIX I CLASSIFICATION OF PURE EXPLOSIVE COMPOUNDS FOR K-9 TRAINING

I PRIMARY EXPLOSIVES

These are most commonly used as initiating compounds and are unlikely to be used alone. They will most commonly be used in conjunction with a larger quantity of high explosive. The exceptions representing a current threat are listed below:

Organic Peroxides

HMTD (hexamethylene triperoxide diamine)

TATP (triacetone triperoxide)

II HIGH AND LOW EXPLOSIVES

The following represent the most commonly encountered explosives for each chemical family and the highest current threat:

<u>1. Nitro Compounds:</u>	<u>TRAINING SAMPLE SOURCE</u>
A. aliphatic nitro compounds:	
nitromethane	Reagent Chemical
B. aromatic nitro compounds:	
nitrobenzene	Reagent Chemical
TNT, DNT	Reagent Chemical
picric acid	Reagent Chemical
<u>2. Nitrate esters:</u>	
methyl nitrate	available?
NG	Pharmaceutical
EGDN, DEGDN	Reagent Chemical**
MTN	Reagent Chemical**
PETN	Det cord
nitrocellulose	single base smokeless powder
<u>3. Nitramines:</u>	
methylamine nitrate	Reagent Chemical**
tetryl	Reagent Chemical
RDX	Reagent Chemical**
HMX	Reagent Chemical**

4. Acid salts:

ammonium nitrate	Reagent Chemical
sodium nitrate*	Reagent Chemical
potassium nitrate*	Reagent Chemical
ammonium perchlorate	Reagent Chemical
potassium perchlorate*	Reagent Chemical
ammonium chlorate*	Reagent Chemical
sodium chlorate*	Reagent Chemical
potassium chlorate*	Reagent Chemical

***NOTE:** not explosives by themselves, but explosives in combination with other compounds.

****NOTE:** available in desensitized form from explosives manufacturers.

VAPOR PRECONCENTRATION IN THE DETECTION OF EXPLOSIVES BY ANIMALS IN AN AUTOMATED SETTING

GERALD B. BIEDERMAN

University of Toronto
Department of Psychology and Division of Life Sciences
Scarborough Campus
Scarborough, Ontario
M1C 1A4 Canada

ABSTRACT. Gerbils were trained to detect C4, Deta Sheet, or Semtex by means of an automated vapor injection system following pretraining with a passive vapor exposure device as in Biederman (1990). Half the animals were then trained using the vapor injection system with a preconcentrator in the target flow, while the other animals received no preconcentration. The results showed that the use of the preconcentrator significantly lowered false alarms (increased correct rejections) in the experimental group. The false alarm rate was significantly higher in a control group detecting explosives without the use of the preconcentrator. The preconcentrator may have also had a positive effect on correct detection of explosives vapor. Further increases in the sensitivity of this system using preconcentration is discussed in combination with other strategies.

In a recent study (Biederman, 1990), gerbils were trained to detect explosives in an automated laboratory setting in order to confirm previous work indicating that detection of the explosive C4 had taken place. The possibility that C4 had been contaminated with EGDN prompted this reexamination. Samples of C4 uncontaminated with EGDN and separate samples tagged with EGDN were used. In addition, two other plastic explosives -- Semtex, currently suspected in recent terrorist incidents, and Deta Sheet (also known as sheet PETN) -- were also used in detection training. Each experimental animal was able to detect each of the four explosives in a short-duration training experiment. Animals were able to detect C4 (in pure and EGDN-tagged forms), Deta Sheet, and were readily able to detect Semtex, but the correct rejection rate (percentage correct when target was not present: H^- , negative hits) was relatively low, C4 (pure): 57 ± 2.0 , C4 (tagged): 60 ± 2.2 , Deta Sheet: 52 ± 2.3 , and Semtex: 51 ± 2.5 .

The purpose of the present study was to improve the level of negative hits by increasing the number of training trials in the vapor delivery method used by Biederman (1990), and by using a vapor injector delivery system with a preconcentrator. Elias (1992) and Krzymien (1992) have suggested a method whereby a metal wire coil is inserted in the airflow and acts as a preconcentrator when a current passed through the coil releases target material that presumably has adhered to the surface of the metal.

Method

SUBJECTS

Six adult male gerbils *Meriones unguiculatus* from a colony at Scarborough Campus.

University of Toronto were used. Each gerbil was housed in a separate home cage and was maintained on an *ad libitum* food (rat laboratory chow) and water schedule.

TARGET SAMPLES

Samples of *C4* [91% RDX (cyclotrimethylenetrinitramine), 2.1% polyisobutylene, 1.6% motor oil, 5.3% Di-(2-ethylhexyl) sebacate], *Semtex H* [min 21.5% RDX, max 64.5% PETN (pentaerythrite tetranitrate), 14% binder--styrene/butadiene rubber and mineral oil], and *Deta Sheet* (63% PETN + pyrocellulose and plasticizer) were provided in separate containers by the National Aeronautical Establishment, National Research Council of Canada. These samples were shaped into 2-cm squares using autoclaved instruments.

APPARATUS

Detection Chamber. A commercial experimental rat station with automate programming equipment was modified with a small two-lever gerbil response chamber with an air inlet (as in Biederman, 1990). This chamber (20 cm X 20 cm X 15 cm) had a 5-cm barred opening centered between the response levers, about 1.5 cm above the floor grid. Explosives vapor was transmitted from an automated vapor delivery device through the 1.5-cm opening in the detection chamber. A harmless 0.5 mA shock was delivered by means of the floor grids. The polarity of the grids was rapidly and randomly scrambled through a standard commercial shock generator-grid scrambler. The detection chamber was housed within a sound-attenuating, ventilated environmental chest.

Pretraining Vapor Delivery System. For the first phase of this experiment, the vapor delivery device consisted of a machined stainless steel cylinder with a 3-cm square opening drilled through a cross section with a sliding machined stainless steel metal bell which could drop over the cylinder completely sealing the opening (Biederman, 1990). The target sample was placed within this opening using forceps to position each sample. The two parts were fitted as closely as possible to slide without lubrication (machined to 0.0001 in. tolerance). A solenoid lifted and dropped this two-part system, with an identical solenoid adjacent to the operating solenoid to provide similar operating noises. When a new target was to be placed in the system, the sliding bell and the sample container were disassembled, cleaned with alcohol, autoclaved and reassembled.

Vapor Injector Training System. The vapor injection has been described elsewhere (Biederman, 1977b); briefly, this device consists of a carrier compressed air flow through a Matheson No. 602 flowmeter, set at a flow rate of 200 cc/min and an injected flow through a Matheson 600 flowmeter, set at a flow rate of 80 cc/min. A continuous compressed air carrier flow from the vapor injector was delivered to the opening of the teflon preconcentrator tube via a stainless steel tube 100 cm from the vapor source and with a 1 mm inside diameter. The air stream from the stainless steel tube was at a right angle to the opening of the preconcentrator tube described below. Through solenoid valves, injector air was either passed through a glass U-tube containing target material, or through an empty U-tube, and then to the carrier flow.

Preconcentration. A teflon tube, 12.5 cm in length and 5 cm inside diameter, was arranged with an internal grid, 3 x 4 cm, of nichrome monofilament wire (Mikrothal No. 80) arranged in a diagonal pattern (the wire was wrapped in equally spaced turns 10 times around two glass rods), fitted at a 90 degree angle to the tube's length. This device was inserted in the air intake of the experimental chamber.

Data Recording. Positive hits ($H+$) -- where a target vapor is presented and accurately detected, Negative hits ($H-$) -- where a target vapor is not presented and the appropriate response lever is depressed, and the total number of target and no-target presentations were each recorded separately by electromechanical counters.

PROCEDURE

Pretraining. Animals were presented with 50 training trials per session for 35 to 42 daily sessions (see Appendix). Before training began each animal was trained to alternate responses between the response levers to escape the scrambled foot shock delivered through the floor grids. In this pretraining phase the "correct" lever varied randomly. The purpose of this procedure was to discourage lever-preference. A trial began with the operation of one of two solenoids depending upon whether vapor would or would not be presented to the gerbil. At the same time the motivating foot shock was delivered and terminated immediately upon a correct response, or after a correction trial was completed following an error. One lever was associated with positive (vapor-present) trials, and the other with negative trials (vapor absent), counterbalanced across animals. In vapor discrimination training, target trials alternated with non-target trials (i.e., trials in which vapor was delivered or not delivered, respectively) in a prearranged random series which was varied at the beginning of each training session. The randomness of the series was only limited by the requirement that no more than 4 trials of one type be permitted to occur in sequence. All trials were run in complete darkness to eliminate distractions and to prevent the animal from receiving any visual cues from solenoid operation. Previous control tests have indicated that the operation of the solenoids conveyed no useful signals to the detecting animals (Biederman, 1990).

Vapor Injector Training. Nineteen 50-trial sessions using the injector vapor delivery system followed the solenoid pretraining phase. One subject under each target vapor condition was randomly selected to receive preconcentrated vapor (experimental) while the other animal received no preconcentration (control). All other conditions were identical. When appropriate, the injector flow was automatically introduced into the carrier flow. The injector flow had either run through a U-tube containing the equivalent of 2cc of target material or through an empty tube. Eight seconds later, the preconcentrator coil was then heated with a 20V current for a 5-sec period. The footshock began at the end of the coil heating and the animal then selected a lever. A correction procedure was in effect, as in the pretraining trials; that is, a trial was not complete until the correct lever was selected. However, the first lever chosen was designated as the animal's choice for that trial. When the correct lever was selected, the carrier and injector flow and footshock terminated. In control animals the preconcentrator coil was not heated. When target samples were changed, the old U-tube was placed in a sealed container with the ends capped and all metal tubing was discarded and new tubing reinserted. Other metal surfaces were cleaned with alcohol and purged with compressed air for 1 hr before reuse with another explosive.

Results

When the last five sessions of pretraining (baseline) are compared with the last five sessions of training for the three experimental animals, a highly significant improvement is found, $t(2)=9.8$, $p<.005$, in terms of correct identification ($H+$) of the three substances. A somewhat weaker, but still significant, finding for correct identification of the three explosives was also obtained for the unconcentrated controls, $t(2)=5.9$, $p<.025$. It is in the development of correct rejections that the effect of preconcentration may be clearly seen: the experimental

(preconcentrated) groups shows a significant improvement from baseline to final sessions, $t(2)=3.4$, $p<.05$, but there is no improvement in correct rejections for the unconcentrated group, $t(2)<1$. There is a significant difference between the final sessions for experimental and control animals in terms of correct rejections, $t(4)=2.2$, $p<.05$. These comparisons and the means of groups are shown in Table 1.

Discussion

The data show that there is a significant percentage increment in detection of the target materials from baseline (last five sessions of pretraining) to the last five sessions of injector training with or without preconcentration, but that negative hits [the reciprocal of false alarms, (F/A)] are significantly facilitated with preconcentration. The explanation for these findings highlights the differences between this "biological" detector and electronic devices using physical and/or chemical transducers in their detection systems. In the latter, one would clearly expect that positive hits would be facilitated by preconcentration. How is it that the present system shows an apparently paradoxical finding?

First, the pretraining arrangements are "noisy" in that incidental amounts of target material may accumulate on the metal and plastic surfaces of the detection chamber when the target is exposed to an air flow. In signal detection terms, the difference (d') between the distributions of noise (n) and signal plus noise ($s+n$) is small. This would account for the relatively insensitive performance in this phase (weak $H+$ percentage, high F/A). The use of the injector, while obviously lowering the absolute concentration of target material at the detection chamber, provides a relatively clean context so that d' is actually greater. Second, the preconcentrator which presumably ejects collected target material in a burst, most likely provides a characteristic odor-package for the detecting animal which heightens the discriminability of (n) and ($s+n$) events. Although there is background target material present during preconcentrator trials, the difference between the two types of trial may become significantly easier to detect.

Considering the very low concentration of target material in the detection chamber during positive trials in the vapor injection phase, one may reasonably argue that this system is actually extremely sensitive, but that residual material in the detection environment reduces the apparent sensitivity. How could the apparent sensitivity be improved?

First, *preconcentration* should routinely be used and efficient and optimal coil designs should be determined.

Second, all materials in the detection chambers used to house animals should be composed of materials that would make traces of residual explosives adhering to surfaces less likely. The surfaces should be supplied with a heating element so that at the completion of a detection trial the surfaces and the detection environment could be effectively purged.

Third, the ratio of positive to negative targets *during training* should be low, that is, relatively few targets should be embedded in a large number of blank trials to attempt to emulate a field detection situation. One problem which arises is that as the animals become more sensitive to the target vapor, the greater is the chance of their detecting trace amounts of vapor in their immediate environment. Correct negative detection is weakened if 50% positive and 50% negative trials are presented, as in the present experiment. This is because vapor is injected on average on every other trial, increasing the opportunity for traces of residual explosives to adhere to the surfaces of the detection chamber.

Fourth, a rapid and total changeover of air in the detection chamber should be routinely performed in intertrial intervals. This type of purging is commonly performed using electronics detectors, and is necessary to lower the F/A rate.

Finally, a two (or more)-animal detection system (with independent and separated detection

chambers) should be considered. In such a system, a positive hit is indicated only when both animals are in agreement. In the case of a two-animal system a 15% false alarm rate would fall to the joint probability level of a false alarm (2%), while the positive hit rate would not fall below acceptable levels -- that is the miss rate would not rise substantially. In field preparations, miss rates below 5% have been reported (e.g., Biederman, 1976). If that level of misses were combined with a 15% false alarm rate, the use of a two-animal detector system would result in a 95% positive hit rate falling to no less than 90%.

Conclusions

Previous research (Biederman, 1974; 1977a; 1977b; 1990; Elias, 1975; Markham, 1977) has described the detection of trace vapors by small animals in automated systems. These studies have indicated certain potential advantages in contrast to existing electronics detection method and in contrast to the use of drugs or explosives sniffing dogs. These advantages include low cost, very rapid detection and (in contrast to dog use) constant motivation with the potential of continuous surveillance in a field detection situation. The current and previous evidence showing that small animal systems can readily detect plastic explosives strongly suggests that this cost-effective system should be adequately configured with a preconcentration device and a detection chamber that can be effectively purged after each detection trial, and then tested in a field context with a full assessment of false alarm rates.

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TABLE 1. Mean percent correct for positive hits (H+) and correct rejections (H-) during last five pretraining sessions (Baseline) and last five vapor injection training sessions (Posttest) in preconcentrated and unconcentrated vapor detection

	Baseline	Posttest	
	H+	H+	
Preconcentrated			
C4	62	86	
Deta Sheet	67	85	
Semtex	67	85	
	(M=65)----.995----(M=85)		
Unpreconcentrated			
C4	65	74	
Deta Sheet	70	82	
Semtex	68	85	
	(M=67)----.975----(M=80)		
<hr/>			
	H-	H-	
Preconcentrated			
C4	59	66	
Deta Sheet	64	77	
Semtex	58	78	
	(M=61)----.95----(M=74) --		
Unpreconcentrated			
C4	60	68	.95
Deta Sheet	69	61	
Semtex	64	64	
	(M=64)	(M=64) --	

Percentages between dashed lines indicate confidence levels for significantly different comparisons.

Appendix

ANIMAL 1

TARGET C4 (EXPERIMENTAL)

Session 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

%H+ 46 56 56 58 67 65 63 60 71 83 67 56 71 60 67 60 58 68 78 63

%H- 46 40 39 38 46 63 54 40 38 44 52 56 54 56 46 52 63 60 56 50

21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40

%H+ 72 50 58 60 62 68 72 71 65 76 59 65 68 67 64 63 56 50 62 71

%H- 48 58 62 60 58 56 56 58 63 52 61 59 60 62 60 54 64 62 58 62

41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61

|-----Preconcentrated Injector Trials -----|

%H+ 62 64 68 66 75 76 72 75 76 76 80 74 72 80 87 80 86 84 84 87 88

%H- 63 52 60 60 53 60 68 57 68 66 72 78 72 80 69 72 66 60 72 61 72

ANIMAL 2

TARGET C4 (CONTROL)

Session 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

%H+ 42 44 43 35 54 48 52 57 56 82 80 69 75 76 75 73 78 73 60 70

%H- 38 40 44 50 31 52 52 56 57 46 48 54 46 56 54 54 52 63 72 65

21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40

%H+ 72 71 71 72 78 74 77 79 69 68 64 72 71 59 65 68 58 62 68 67

%H- 56 62 58 64 67 70 63 56 54 48 60 60 61 74 52 52 62 71 60 54

41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59

|-----Unconcentrated Injector Trials -----|

%H+ 68 72 72 64 72 76 68 75 72 60 72 65 64 78 70 72 73 80 76

%H- 64 60 64 64 68 58 64 65 64 60 64 53 72 68 73 68 66 68 64

ANIMAL 3

TARGET DETA SHEET (EXPERIMENTAL)

Session	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
%H+	48	83	72	52	48	56	58	60	58	65	67	62	65	67	60	65	60	64	63	63
%H-	32	04	08	57	56	60	58	48	42	44	50	63	52	58	48	52	52	60	61	61
	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
%H+	64	68	68	75	76	79	69	80	73	72	75	73	68	75	68	72	67	56	64	75
%H-	60	56	60	65	68	65	71	20	67	68	62	71	72	69	64	64	69	68	60	62
	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	
	-----Preconcentrated Injector Trials -----																			
%H+	72	65	76	80	80	77	80	80	84	88	88	92	96	88	87	72	80	96	88	
%H-	72	75	72	68	76	91	80	80	80	84	84	76	72	86	80	72	75	80	80	

ANIMAL 4

TARGET DETA SHEET (CONTROL)

Session	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
%H+	50	32	42	44	44	48	50	52	58	56	48	54	58	67	60	64	58	52	57	64
%H-	46	48	58	60	74	76	75	67	69	60	60	58	54	50	60	56	67	65	68	65
	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	
%H+	65	64	80	84	85	84	80	69	62	68	60	67	64	60	71	64	62	68	83	
%H-	46	60	60	64	71	68	72	71	58	64	64	65	68	64	69	60	79	72	65	
	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	
	-----Unconcentrated Injector Trials -----																			
%H+	72	76	80	76	80	80	76	76	80	72	80	88	80	72	80	80	84	84	80	
%H-	68	68	72	68	68	68	68	64	72	64	64	64	64	68	64	60	52	60	68	

ANIMAL 5

TARGET SEMTEX (EXPERIMENTAL)

Session 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

%H+ 40 46 40 37 36 40 35 38 50 52 58 52 56 48 54 60 64 58 52 63

%H- 52 46 48 61 60 56 58 62 62 68 69 70 60 72 69 72 68 69 56 58

21 22 23 24 25 26 27 28 29 30 31 32 33 34 35

%H+ 75 76 69 68 71 72 73 60 64 71 67 60 64 71 72

%H- 62 64 67 60 69 52 57 60 60 58 38 56 64 68 64

36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54

|-----Preconcentrated Injector Trials -----|

%H+ 72 80 83 84 76 84 91 84 84 80 80 88 84 88 84 84 88 84 84

%H- 76 80 80 79 80 72 80 76 80 72 80 76 80 84 72 88 76 80 76

ANIMAL 6

TARGET SEMTEX (CONTROL)

Session 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

%H+ 46 48 52 50 54 65 65 60 64 71 64 64 63 69 76 69 65 64 72 76

%H- 42 48 41 62 50 50 54 52 60 54 63 60 64 67 60 63 67 68 60 64

21 22 23 24 25 26 27 28 29 30 31 32 33 34 35

%H+ 81 80 73 71 67 65 68 75 73 72 71 54 48 68 68

%H- 67 68 71 69 70 58 64 62 63 60 60 58 68 68 64

36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54

|-----Unconcentrated Injector Trials -----|

%H+ 76 87 80 84 88 84 84 84 80 80 72 80 84 80 84 80 88 84 88

%H- 68 65 64 64 64 68 60 64 68 72 72 64 64 64 68 64 64 64 60

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VAPOR GENERATION FOR USE IN EXPLOSIVE PORTAL DETECTION DEVICES

by

Edward E. A. Bromberg
Daniel Dussault
Stephen MacDonald
Thermedics Detection, Inc.
Woburn, MA 01888
USA

William A. Curby
FAA Aviation Security
Atlantic City, NJ 08405
USA

ABSTRACT. In order to evaluate portal explosive detection devices properly, a means of generating a known vapor sample of the different explosives and a surrogate for bulk explosives are required. What is described is the design and evaluation of a secondary vapor generation source that has proven to be effective in calibrating both the absolute sensitivity and the spacial distribution sensitivity of a portal explosives device. In addition, bulk explosives surrogates will be described that can safely be used to effectively evaluate a portal's ability to actually find hidden explosives.

1. Introduction

In the development of portal explosive detection systems, a detailed and rigorous testing protocol is required for the eventual evaluation of the effectiveness of the device. Since it is often not possible to bring large quantities of explosives to a site where large scale testing and evaluation is being performed on the portal, it is desirable to have a bulk explosive substitute. This report contains a description and evaluation of a pulsed explosive vapor source that generates a known amount of explosive vapor over a short period of time (of order of seconds.) It also contains a description and evaluation of two types of bulk explosive substitutes, that is substances that contain real explosives, but in such low amounts that they can safely be carried by the test subject yet still give an alarm when sampled by the explosive detector. The pulsed vapor source would be used to demonstrate that the device works under ideal conditions, to quantify the absolute sensitivity, to determine the collection efficiency of the sample collection train, and to determine any changes in sensitivity when the explosives are placed in different positions within the portal. The bulk explosive substitutes could be used on a known fraction of a large number of subjects being tested in the portal device to determine both hit rates and false alarm rates. The bulk explosive substitute could also be used as a simple "front-end" test to demonstrate that a unit is operational. Additionally these explosive generators and substitutes should prove useful during the development stage of explosive detection systems by providing a quick and easy evaluation as to whether changes in the system lead to improvements.

In this discussion, it is assumed that the explosives will be present as both vapors and particles by the time it reaches the analyzer, irrespective of how it is generated. No assumption will be made as to the exact mechanism of collection. Since explosive detection devices used to screen

passenger etc, are semi-quantitative in nature, there is no need to determine the response to the explosives quantitatively. Thus, the techniques described below are not meant to be accurate to a few percent, but rather are semi-quantitative in nature.

2. Pulsed Vapor Generator

2.1 GENERAL DISCUSSION

This generator is based upon the sampling preconcentrating collector developed for the Thermedics Detection, Inc. EGIS, which is described by Rounbehler et al (1991). This mobile explosive detection system is based upon a high speed chromatograph with a chemiluminescence detector and uses a collector to pre-concentrate the sample. In use, the sample is sucked through the collector, and a fraction of the vapors and particles stick to the surface. The collector is then connected to the heated chemical analysis part of the unit. Once the collector is connected to the chemistry module, the ribbon collector is heated rapidly to the desired temperature, and the explosive molecules that have accumulated on the ribbon surface vaporize and are transferred to the chemistry module where they are analyzed.

To calibrate the device, a known amount of different explosive mixtures in solution is injected onto the collector. The collector is then connected to the analysis section, fired, and the vapors are then analyzed. In this manner the retention time, as well as the signal strength per unit amount of explosives can be calibrated. From this signal strength per unit amount of explosives, the approximate sensitivity of the unit can be determined. The process of transferring the explosives from the collector to the chemistry module is referred to as desorbing the collector. Experiments on EGIS have demonstrated that greater than 90% of the explosives injected onto the collector are desorbed in the first 2 seconds of firing.

What is proposed, and has been demonstrated to work, is to take this same collector, perform an injection of a known amount of explosives onto the collector, and then to fire the collector in a controlled manner directly into the portal while the device is performing a sample.

2.2 DESCRIPTION AND USE OF PULSED VAPOR GENERATOR

Figure 1 is a sketch of this device. It consists of the collector, a back plate with O-rings that seals against the collector, a source of desorb air, a heated snout, and mounting hardware. The drive circuitry to heat the ribbon, the temperature controller for the snout, and an electrically controlled solenoid to turn the air flow on when the collector is being heated are not shown. This collector is made of a metal ribbon that is wound around a hub. The inner hub is about .75 cm in diameter. The inner diameter of the outer ring of the collector is about 1.5 cm. The height of the wound collector is about 1 cm. The outer ring has an outer diameter of about 6 cm. On the face of the outer ring are four insulated electrical pins that are electrically connected to the coil, and are used for heating and measuring the temperature of the ribbon of the coil. A manual clamp is used to hold the collector in place and sealed tightly between the sealing back plate and the heated snout. In typical use, the collector is fired throughout the duration of the sampling time. The back plate and snout are required in order to get the proper directed air flow across the collector, and to get the proper electrical connections. The snout is heated to avoid condensation of explosives. Typical desorb flow rates are 1 liter per minute.

The spacial distribution of the portal system is determined by positioning this pulsed vapor

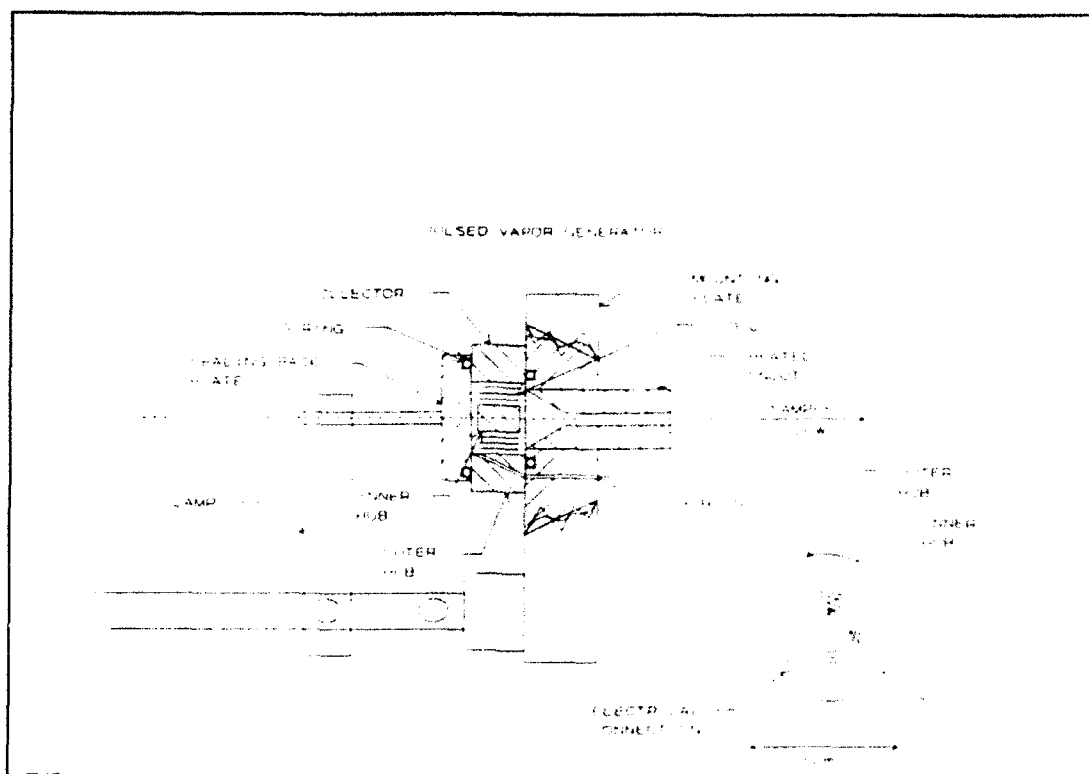


Figure 1 - Pulse vapor generator

generator in different positions within the portal.

Standard solutions desorbed directly into the analysis section gives a calibrated response for the analysis section. Then by using the same, or a similar calibrated solution in the pulsed vapor generator in the portal, one can calculate an effective efficiency ratio, i.e., what fraction of the explosives that are released into the portal are eventually detected by the analysis component of the system. This calculation is valid since it has been demonstrated that in excess of 90% of the explosive material injected onto the coil is desorbed into the portal. This demonstration is performed by desorbing the collector directly into the chemistry module immediately after desorbing into the portal. The remnant found is less than 1%.

In order to use this device, the collector is manually removed from the pulsed vapor injector assembly of Figure 1. Using a syringe, a known amount of solution, typically 1 - 10 μ l, of known concentration is injected onto the coils of the collector. The collector is then replaced into the pulsed vapor injector assembly, the assembly placed in the desired location of the portal. In these experiments, the sampling mode of the portal is then turned on, and the pulse injector is fired simultaneously under computer control. The collected sample is then analyzed.

The portal, see Figure 2, used in these tests was a walk-in walk-out booth with a floor, ceiling, and three sides, about .75 meters wide, 1.25 meters deep and 2.5 meters high. On the side opposite the open side there are five intake ports. Each one a rectangular funnel, 40 cm high by 25 cm wide, connected to a 8 cm diameter pipe. The center of the five funnels are at 20, 60, 100, 140 and 180 cm measured from the floor. The five pipes are connected at a mixing box. During sampling a large blower sucks room air through the open side of the portal around the subject, through the five funnels, into the mixing box, and finally to the exhaust. The sample that

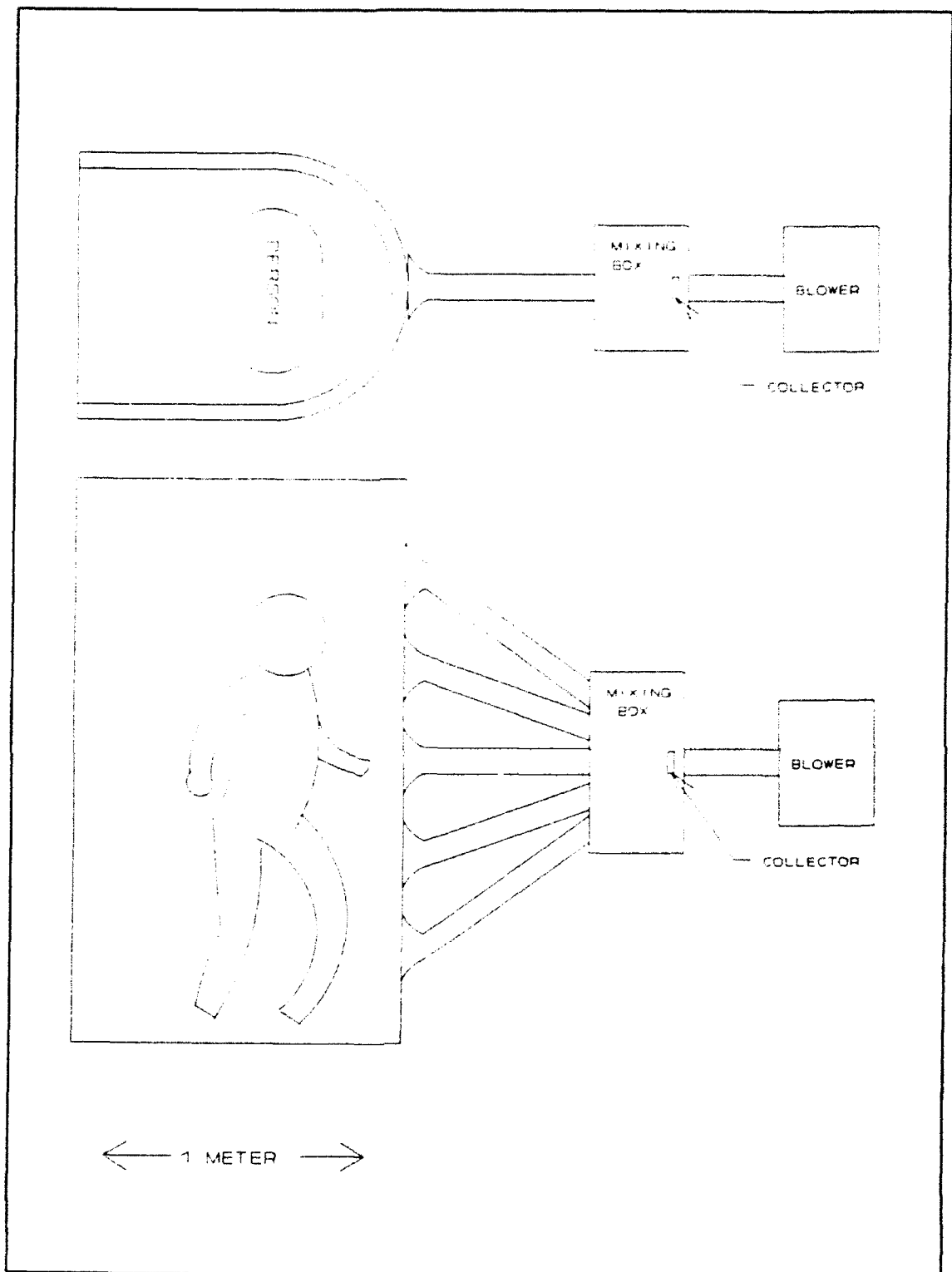


Figure 2 - Sketch of portal layout.

is used is removed from the mixing box.

2.3 DATA FORMAT

Figure 3 shows a typical chromatogram obtained in these experiments. The X axis represents time in units of milliseconds. The Y axis represents relative intensity. The number on the top of the Y axis is the maximum relative intensity, while the number listed to the left of the Y axis is an attenuation factor. A "P" on the chromatogram represents a peak found by the software, while an "H", hit, on the chromatogram represents a peak found by the software within the time window of retention times of the explosives for which the system has been calibrated. The lines labeled one through six indicate the retention times expected for explosives one through six: EGDN, NG, DNT, TNT, PETN, and RDX respectively.

2.4 EXPERIMENTAL RESULTS

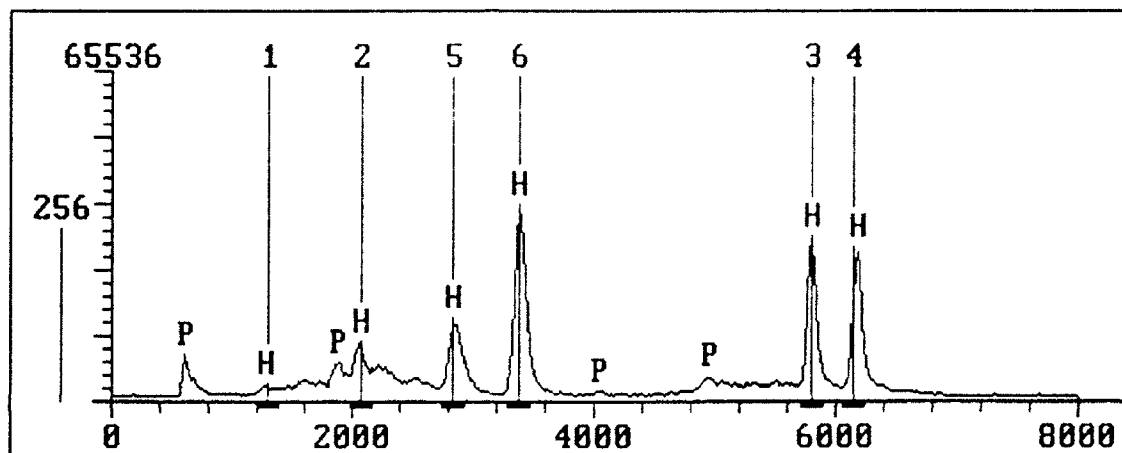


Figure 3 - Typical result from the pulsed vapor injector.

Figure 3 shows a typical chromatogram using the pulsed vapor injector. This particular chromatogram was obtained from an injection of a mix of the explosives onto the collector. This injection was made near the center intake funnel of the portal. By comparing the results of this injection with the known sensitivity of the analysis device, it is calculated that the collection efficiency is about 1:500 for the configuration tested. This number is reasonable, since in the configuration of this test, only about 1/50 of the sample was intersected by the sampling collector, and the particular sampling collector used has a collection efficiency of about 10%. There is a finite acceptable flow through the sampling collector. Since it is required to completely purge the portal in the time frame of the analysis time, a much larger flow through the portal is required than can be reasonably sampled by the collector, thus only 1/50 of the sample is collected for the configuration reported here.

Further tests that were performed with the device were to use successive dilutions of the injection solution to both determine the linearity of the system and the lower detectable limit. Figure 4 shows the results of the successive dilution tests. The lines are a linear regression match to the experimental values, which are indicated by the symbols listed in the figure. It is seen from this figure that the system has a linear response. The fact that the pulsed vapor generator leads

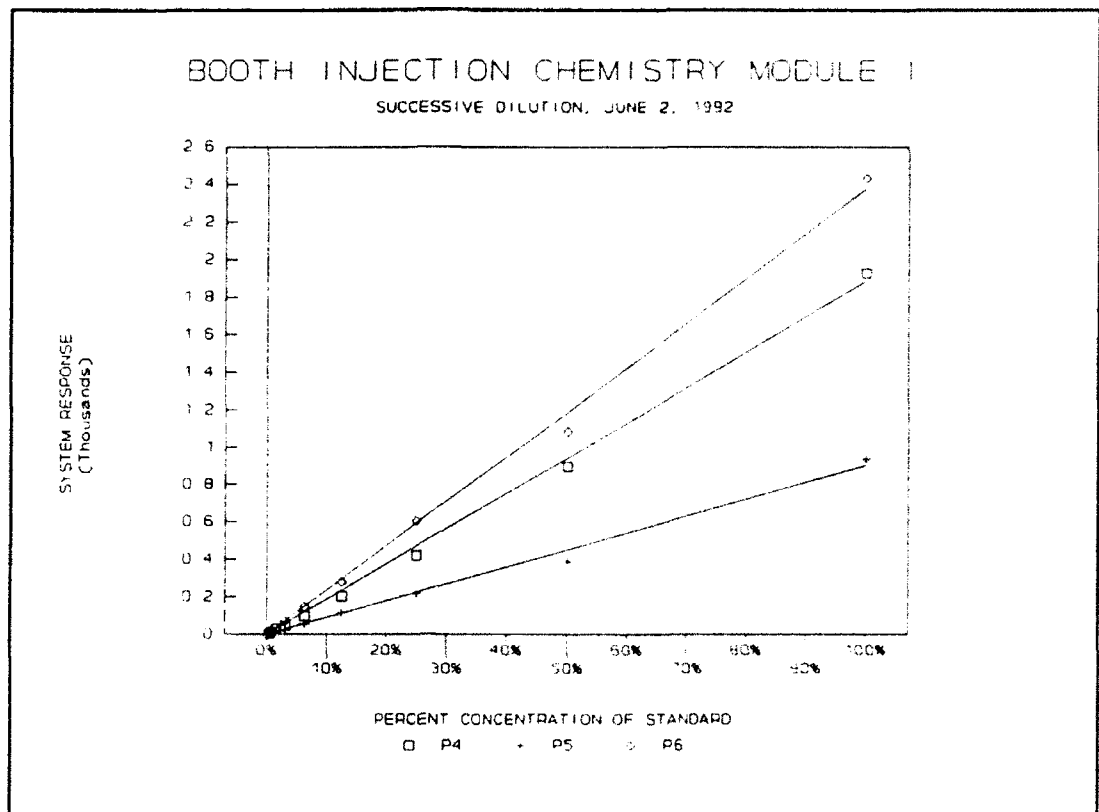


Figure 4 - Response to successive dilution of the vapor injection solutions.

to linear results is an indication that it is well behaved and predictable.

A second test performed, demonstrating the use of the generator in determining the positional sensitivity of the portal, was to place the source in different positions within the portal. These positions, in front of the individual input funnels, included top, upper middle, middle, lower middle, and bottom of the portal. Each reported test point of Figure 5 is the result of the average of five runs. From this figure it is seen that for the portal configuration tested, the peak spacial efficiency occurs at the middle of the portal, with a drop in collection efficiency at the top and bottom of the portal. Since this drop is typically less than 30% it is not of major concern, and indicates that the mixing box does indeed mix the sample adequately.

These results are reasonable when compared to the calculated expected results given above, and thus lead to the conclusion that this pulse vapor injector can be used as a method of quantifying the ultimate sensitivity and spacial sensitivity of a portal device under controlled conditions. That is, one can use this method to inject a known amount of explosives into the portal while it is sampling, and by observing the results can determine the detection limits under these ideal conditions.

Other methods of introducing pulses of vapors can also be used. A few tests were performed using a temperature stabilized heated plate in the portal, to which a measured amount of explosive solution was added. Results similar to those of Figure 3 were obtained, however, the reproducibility was not nearly as good when compared to the pulsed vapor generator of Figure 1.

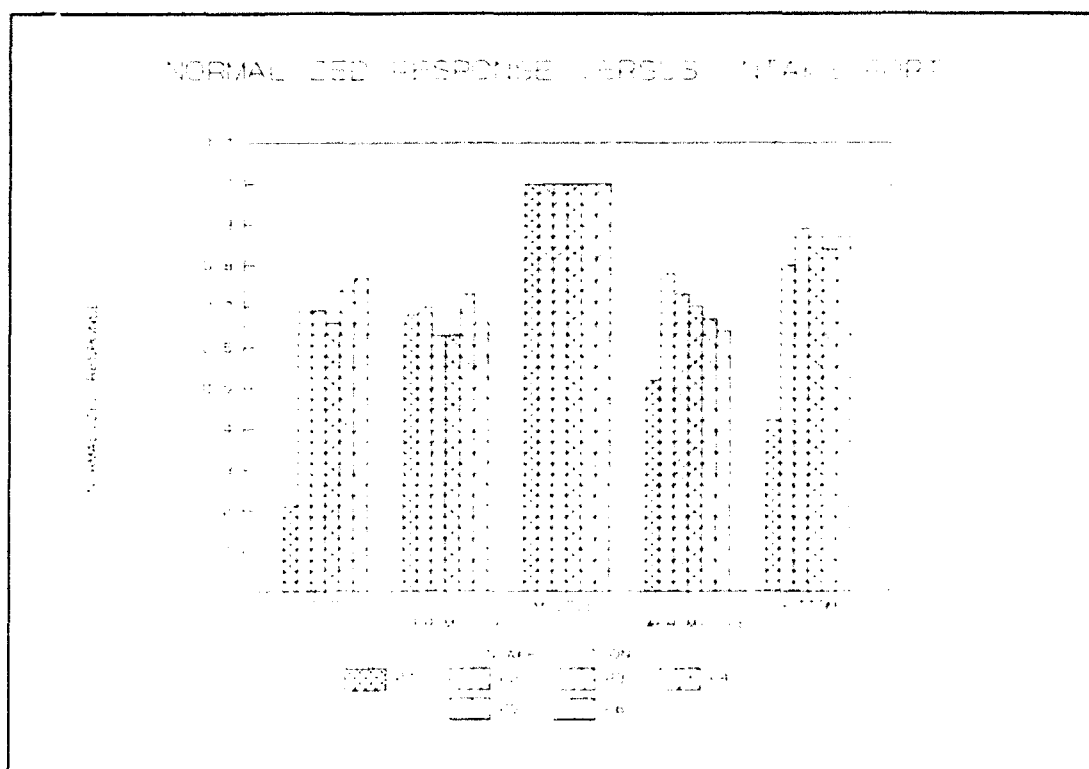


Figure 5 - Normalized signal response as a function of explosive and portal position.

3. Patch Bulk Explosive Substitute

3.1 GENERAL DISCUSSION

The field test operational portion of a typical test protocol would usually include installing the portal in a high traffic public area, such as an airline terminal. A large number of passengers would then be requested to walk into the portal device in order to obtain both the reaction of the traveling public to the device, as well as to see the unit's response to the typical subject. This response would lead to an evaluation of the false positive alarm rate of the unit with a large sample population. However, a proper determination of the false positive alarm rate can be made only if the alarm setting is set sensitive enough to pick up an alarm when required. Therefore, interspersed with random passengers, one would desire subjects that are carrying explosives. This guarantees that the alarm level is set correctly and additionally leads to a hit rate and false negative rate for the device. From a safety and psychological point of view it is clear that the interspersed subjects can not be carrying any significant amount of explosives. Since these devices are not bulk detectors, but rather vapor or particulate detection devices, the generation of a "test atmosphere" is less dependent upon the size as opposed to placement, contamination and equilibrium conditions of the test sample. Therefore, a very small amount of explosives (below a milligram,) which can be spread very thin, can be as effective a source as detonation quantities. Certainly if the device is capable of detection of milligram quantities on a person it is capable of detection levels of explosives that are capable of detonation.

Based upon the above considerations, a bulk explosive substitute was developed. Patches of

materials such as a 10 x 10 centimeter paper towel, filter paper or sterile gauze pad, to which a known amount of a very dilute solution of a mixture of explosives or a single explosive is added. The solvent is then allowed to evaporate, and the bulk explosive substitute is then available for use. Since very small amounts of explosives are being used, and since it is dispersed over a very large surface area, there is no possibility of detonation of the patch with the explosives added. Once prepared these bulk explosive substitutes can be stored in a vapor tight container to keep the volatile components from evaporating. In use, these small patch bulk explosive substitutes can be hidden on the prospective subjects, and after different "soak times" the subjects can then present themselves along with the general public going through the portal. These tests should be performed double blind, with the portal operator not knowing who is part of the general public, and who has a patch hidden. Additionally, the subjects with the patches should not know whether the patch had explosives added to it or only pure solvent.

3.2 Experimental Results

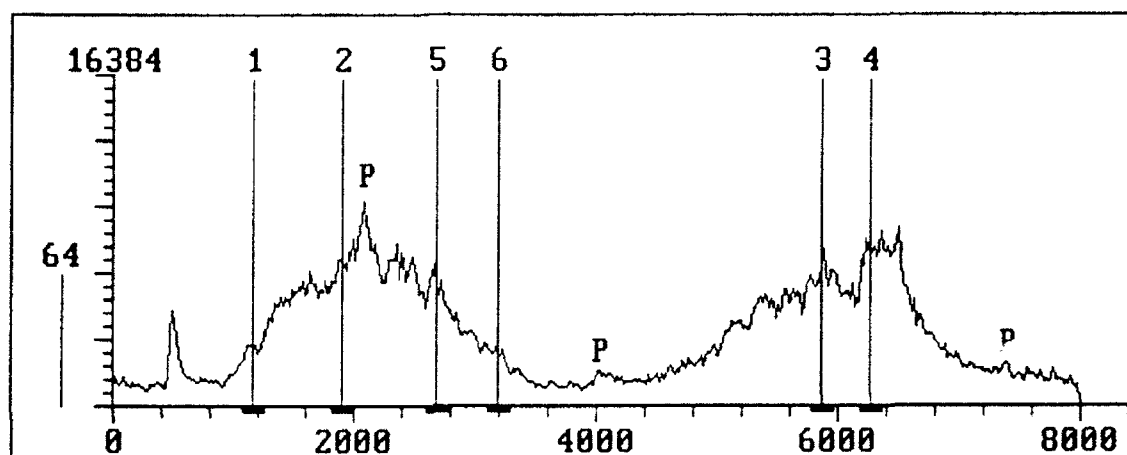


Figure 6 - Typical blank with a subject in portal.

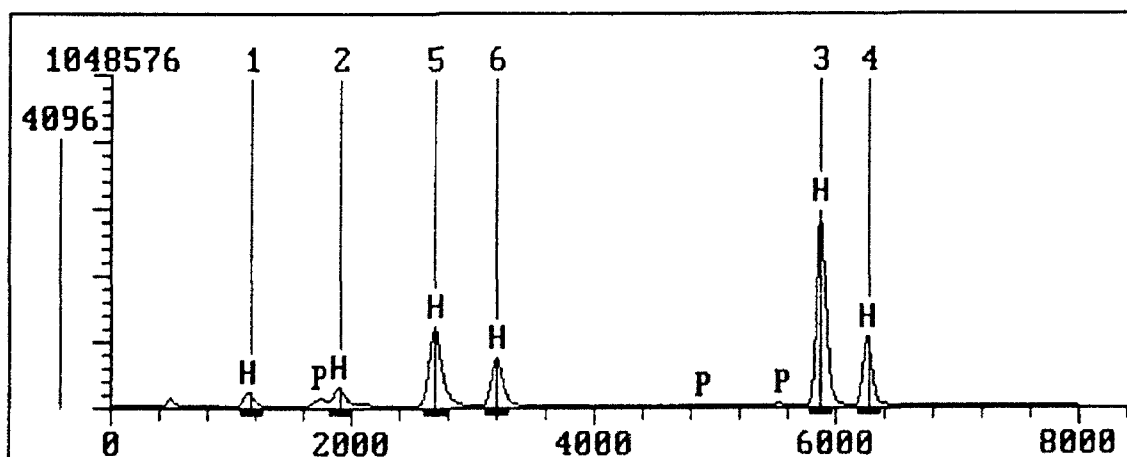


Figure 7 - Typical response of subject with patch containing a mix of 6 explosives.

In performing the evaluation tests in the laboratory the following procedures were used. First a blank was performed on the portal by itself, then on the portal with a subject inside to see if there was any residual background. Only after the portal and the subject were demonstrated to be clean were the patches placed on the subject, either clipped to the outside of their clothing, or hidden in a pocket. Figure 6 shows the typical results of a blank performed on a subject inside the portal. The subjects were then sampled after different soak times after the addition of the patches. Figure 7 shows the results of a typical run with a subject in the portal with a patch that contains a mixture of 6 explosives. This mixture was essentially equimolar. It should be noted that the volatile explosives (the first and second peaks) have relatively weak signals. This is most likely due to the fact that in the time allotted to evaporate the solvent as well as soak time on the subject, significant amounts of the high vapor pressure materials evaporated.

4. Wrapper Bulk Explosive Substitute

4.1 GENERAL DISCUSSION

Since these detection systems are not bulk detectors, the amount of explosives present is not the factor in determining the probability of detection, but rather if the explosives are present in a detectable form. Any way of introducing small amounts of explosives in a reproducible and detectable form can form the basis of a bulk explosive substitute. A second explosive bulk substitute that has been investigated as part of this work are wrappers. Two types of wrappers have been used. The first are the actual wrappers that the explosives were packaged in, the second are different fabric materials that were wrapped around different explosives, allowed to sit, and then unwrapped. The wrappers are then placed in subjects pockets, hidden under shirts or sometimes just held up in front of the subject while being sampled in the portal.

4.2 EXPERIMENTAL RESULTS

Figure 8 shows the results of a C-4 (RDX containing) wrapper test. This particular wrapper is one that had been removed from a block of C-4 at least three years ago. As seen in this figure, there is a strong peak at peak 6 position, what one would expect for a C-4 wrapper. Clearly this wrapper is perfectly safe, yet still is an effective method of checking for the effectiveness of the device to detect C-4. Similar results are obtained for different fabric materials that are taken and wrapped around different masses of different explosives.

4.3 DIFFERENCES BETWEEN PATCHES AND WRAPPERS

There are two major differences between patches and wrappers. The wrappers contain the actual explosive material in the format that it is usually present, while the patches contain the pure chemical. On the other hand, the patches are easier and safer to manufacture since only small quantities of explosives are required and they are more reproducible. In manufacturing the patches, the actual explosive chemical is dissolved in solvent. If all materials are weighed carefully, then the concentration of the solution is well defined, and if a known amount of solution is added to the patch, the exact amount of explosive present after the solvent evaporates is known. On the other hand the wrappers come in close contact with the explosive, and a certain amount of explosive is transferred from the explosive to the wrapper. This transfer of explosives

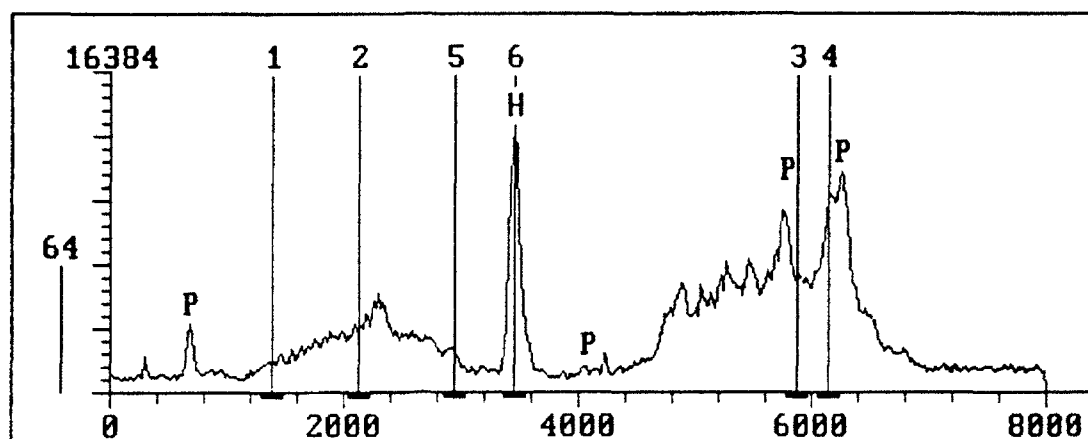


Figure 8 - Subject in portal with C-4 wrapper.

is not reproducible, and thus the results with the wrappers are not as reproducible as that for the patches. However, it is very possible that the binders and oils present in the explosive, has an effect on the ability of the device to find the explosive. The matrix effect of binders and oils is not present in the patches, but is present in the wrappers. Thus the results obtained from the wrappers and patches complement each other.

5 Discussion of Results

5.1 COMPARISON BETWEEN BULK SUBSTITUTES AND ACTUAL EXPLOSIVES

There are subtle differences between actual explosives and the bulk explosive substitutes. Therefore, while the bulk explosive substitutes discussed in this paper are effective substitutes for evaluation of portal explosive detection system, they do not replace the need to test the devices with real explosives. However, the tests with live explosives need not be performed in areas with high densities of people. These tests can be performed off site, with comparisons made between the results with the bulk substitutes and the live explosives. Based upon these comparisons, effective ways of using the bulk explosive substitutes can be developed for each different device. These methods of using the substitutes can then be used in the high traffic areas with confidence.

As part of the evaluation of these bulk explosive substitutes, tests were performed with live explosives. The actual chromatograms obtained are indistinguishable from those obtained with the wrappers. For example the chromatogram shown in Figure 8, for a C-4 wrapper would be indistinguishable from the chromatogram obtained for a subject with hidden C-4.

The protocol for introducing live explosives onto test subjects is a detailed and complicated one and is not addressed here.

5.2 VAPOR VERSUS PARTICLES

Analysis of the results of these tests lead to the conclusion that the mechanism of transport of the sample from the subject to the preconcentrating collector is both vapor and particles. Table 1 lists the equilibrium vapor pressure for the explosives tested for in these tests, see Dionne et al (1986). As seen from this table there is greater than a thousand fold difference in vapor pressure at room

temperature between TNT and RDX, and about a 10,000 difference between DNT and RDX. If the mechanism of transport of the sample to the preconcentrator was purely that of vapor it is expected to see signal response differences for these explosives comparable to the differences in vapor pressure. This is not the observation in comparing the results between DNT, TNT, PETN, and RDX. The results of the highly volatile explosives, EGDN and NG are not considered in this discussion, since in the time frame of these experiments a significant fraction, if not all of these two explosives will have evaporated.

Table 1 - Explosive Equilibrium Vapor Pressure at Room Temperature	
Explosive	PPT(V/V)
EGDN (Peak 1)	100,000,000
NG (Peak 2)	580,000
DNT (Peak 3)	55,700
TNT (Peak 4)	9,400
PETN (Peak 5)	18
RDX (Peak 6)	6

For the case of the experiment of Figure 3, a known amount of a solution, approximately equimolar in concentration, of the different explosives is added to the collector. The collector is then fired at a high enough temperature to effectively vaporize all of the explosives on the collector into the air surrounding the pulse vapor generator. Thus in this case approximately equimolar amounts of all of the explosives are presented to the preconcentrator. As seen from Figure 3, the system response to the four low vapor pressure explosives is similar, within a factor of two. On the other hand in the case of the patches, if the transport mechanism were purely vapor, it is expected that the instrument response should reflect the vapor pressure differences of Table 1. Reference to Figure 7 shows that this is not the case. While the relative system response in Figure 7 is different than that of Figure 3, it is no where near the excess of a thousand fold predicted by the vapor pressures of Table 1. Thus the transport mechanism is other than pure vapor. One mechanism that has been proposed, but not proven, is that the explosives are adsorbed on dust, lint and other similar particles. During sampling it is these particles, along with vapors, that are the active means of transport to the preconcentrating collector.

During the first time the patches were made, they were allowed to dry by sitting in air on a table close by the portal. Portal blanks that were performed immediately after the addition of the explosives showed a very large peak 1 background, that went away when the patches were removed. It is speculated that the high peak one background was due to the peak 1 material evaporating into the air around the portal.

5.3 INTERFERENCES

Any test of an explosive detection device has to include testing for interferences. Tests for

interferences have to be for both positive as well as negative interferences. Ideally the testing for interferences is performed in the presence of explosives since this is the only way one can determine if there is a negative interference. Tests of large numbers of passengers at airports are an effective method for testing many random samples for positive interferences. The patches and wrappers are an effective method for testing for negative interferences. For these negative interference tests large numbers of patches and wrappers are made. To a large fraction of these patches and wrappers, different potential interferences are added. From the statistical response to the bulk explosive substitute without potential interferences to the response to the bulk explosive substitutes with interferences, a negative and positive interferant equivalent for the different potential interferences can be determined.

6 Acknowledgements

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DESIGN CONCEPT: FEMTOGRAM-LEVEL EXPLOSIVES VAPOR GENERATOR

D.P. LUCERO AND S.R. RODER

Lucero and Associates

18421 Cedar Drive

Triangle, Virginia 22172

USA

and

P. JANKOWSKI AND A. MERCADO

FAA Technical Center

Atlantic City Intl. Airport

Atlantic City, New Jersey 08405

USA

ABSTRACT. The evaluation and response calibration of an explosives vapor detection system for a variety of explosives species can be performed by a vapor generator with unique operating specifications and versatility. This design analysis of a vapor generator concept addresses the evaluation and calibration requirements of an explosives vapor detection system alarming on low explosives vapor mass input ($\sim 1 \times 10^{-15}$ to 5×10^{-15} g) for the low vapor pressure explosives.

This concept uses a special-purpose permeation device (a permeation bag), with an explosives vapor emission rate that can be determined gravimetrically with commercial microbalances in 1 to 10 days. A special-purpose thermal chamber contains the bag at a controlled temperature. It uses a porous wall through which carrier air flows and forms a continuously renewed air boundary layer at the porous surface, thus preventing explosives molecule surface adsorption to its walls. Downstream of the chamber and permeation bag, a heated and temperature-controlled tubular membrane precisely extracts explosives vapor molecules from the chamber carrier air stream at a controlled low flow rate. Thereafter, the explosives vapor molecules are transported out of the generator with either a continuous air stream to simulate the explosives vapor concentration in a detection scenario or with a smaller, pulsed gas flow rate to simulate a localized injection of explosives vapor mass adjacent to the detection system. Regardless of the air flow rate, approximately 1×10^{-15} g of explosives vapor molecules are produced by the generator in a 3-s period.

1. Introduction

The performance evaluation and calibration of an explosives vapor detection system for aviation and other security applications can be accomplished with reasonable accuracy by using an explosives vapor generator that simulates, to a practical degree, the critical aspects of a "typical" detection scenario. This includes releasing an explosives vapor mass into the atmosphere at stations simulating the configurational and dimensional relationships of the target

subject and vapor detection system over a time period equivalent to the system sampling or examination time increment. A vapor generator meeting these requirements can be used to evaluate the detection system response and account for sample collection and transport inefficiencies, the preconcentration process, and the detector module response in the overall system performance. Estimates on the required maximum explosives vapor mass input to the atmosphere by the vapor generator range from 1×10^{-15} to 20×10^{-15} g (FAA, 1990; Pate, 1976; Lucero, 1985).

The engineering aspects and constraints ordinarily encountered in designing an ultra-low-level vapor generator are compounded enormously in dealing with explosives vapors. Most of the complications stem from their adsorptive characteristics and, particularly for RDX and PETN, their relatively low vapor pressures (Dionne et al., 1986). Unless the vapor generator is equipped with special features, surface adsorption leads to an unstable or unknown generator output. In addition, the vapor output rate measurement from the explosives vapor source can be a very tedious multistep transaction (Dionne et al., 1986).

Explosives vapor generators generally use "over the surface" type explosives sources (Pella, 1976) in which a small clean air stream flows past a small mass of pure explosive. Usually, the explosives material is contained in a packed column and/or deposited on a surface matrix. The air stream is saturated, at a given equilibrium temperature, with the vapor molecules at the column exit. For example, at 25°C, the equilibrium vapor pressure of RDX is 6 pptv; thus, the air stream RDX concentration is also 6 pptv. A 100-ml/min saturated air stream carries 5.4×10^{-12} g/min of RDX; a vapor detection system sampling for 3 s will ingest 2.7×10^{-13} g. It will ingest 1.2×10^{-12} g and 4.4×10^{-10} g of PETN and TNT, respectively, and larger masses for NG and EGDN for identical conditions.

This explosives vapor mass output is 1 to 5 orders of magnitude larger than the mass input required to simulate a detection scenario. Reductions in the explosives mass generated can possibly be achieved with corresponding reduction in the carrier air stream flow rate and the explosives source temperature. However, because a reduction of several orders of magnitude in explosives vapor concentration is required and, consequently, excessive dilution air flow rates, this approach is unappealing. It is also possible that schemes using saturated air streams together with downstream stream splitting and subsequent stream-rejection and dilution processes (Marshall et al., 1981) can be used to reduce the generator mass output. Success with these schemes depends on the combined stability of several processes for each stage, which can lead to large overall instabilities and errors. It is certain that variable and controlled dilution over wide ranges is required of the primary explosives vapor stream produced by the generator to obtain useful output levels for all explosives species.

The explosives vapor generator described below uses several unique features in the explosives vapor source, pneumatic components, and modules and in using pervaporation techniques to perform controlled and large dilutions. It is presently in the initial development stage at the United States Federal Aviation Administration Technical Center laboratories. Preliminary performance specification goals for the vapor generator are: (1) explosives mass output: 50 fg to 50 pg; (2) pulsed and continuous explosives mass outputs; (3) maximum output instability: $\pm 5\%$ absolute; (4) output gas flow rate: 50 to 1000 ml/min; and (5) explosives mass output traceable to a gravimetric standard. These performance specifications are preliminary and will change as the vapor generator development progresses and will evolve

continually to meet the detection system requirements.

2. FemtoLog

The vapor generator is called FemtoLog for easy reference. It is similar pneumatically to most explosives vapor generators regardless of the vapor source type used (Pella, 1976; Marshall et al., 1981; Lucero, 1976; Lucero, 1971): a vapor source is contained within a temperature-controlled chamber where it emits vapor molecules at a controlled rate as a metered carrier gas stream passes over the source and transports vapor molecules to a vapor detection system. FemtoLog, however, uses a permeation explosives source (a permeation bag), a special-purpose thermal chamber to contain the permeation bag, and a downstream dilution device that delivers explosives vapor masses to a vapor detection system in femtogram quantities in an air stream that can be varied over a wide flow rate range.

The FemtoLog pneumatic configuration and general operation is illustrated by Figure 1. A permeation bag is contained within the thermal chamber at $75^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$. A filtered, scrubbed, and metered room air stream flows into the thermal chamber at $1 \text{ l/min} \pm 0.01 \text{ l/min}$ to the dilution-delivery module through a vent-line scrubber and is returned to the room. As explosives vapor molecules emit from the permeation bag, the carrier air stream transports the molecules into the dilution-delivery module where a second stage dilution process operates on the explosives vapor molecules. All elements of FemtoLog downstream of the thermal chamber are maintained at 150°C .

The dilution-delivery module is basically a temperature-controlled semi-permeable membrane at $150^{\circ}\text{C} \pm 1^{\circ}\text{C}$, which separates the thermal chamber air carrier stream containing the explosives vapor molecules and the dilution-delivery module carrier air stream of Figure 1. Approximately a 1-l/min dilution room air stream flows to the dilution-delivery module and passes over one side of the membrane. The thermal chamber carrier air stream flows past the opposite side of the membrane. A small stream of explosives vapor molecules flows from the thermal chamber air carrier stream, through the membrane by a diffusion process, and into the dilution-delivery module carrier air stream at a rate proportional to the product of the membrane permeation conductance and the explosives vapor partial pressure or concentration of the thermal chamber carrier stream (Barrer, 1951).

Thus, two stages, the bag and the membrane, are used to produce an air stream containing controlled and ultra-low-level concentrations (Lucero, 1976) and masses of explosives vapor molecules. For example, FemtoLog operating with an RDX permeation bag as described above and with a dilution-delivery module using a carrier air stream at a total 1-l/min flow rate yields a 2×10^{-3} pptv output concentration or a 2×10^{-14} g/min RDX mass flow rate. A vapor detection system ingesting the entire dilution-delivery module carrier air stream for 3 s will ingest 1×10^{-15} g of RDX. An identical explosives vapor mass would be ingested regardless of the dilution-delivery module carrier air stream flow rate. The explosives vapor molecule mass flow rate generated by FemtoLog is

$$M_e = k_p W/MQ_c \quad (1)$$

where

M_e = explosives vapor output mass flow rate, g/min;

k_p = mass constant, g-ml/mole-min;

Q_c = thermal chamber carrier air stream flow rate, ml/min;

W = permeation bag explosives vapor emission rate, g/min; and

M = explosives vapor molecular weight, g/mole.

The explosives vapor molecule concentration of the FemtoLog output stream is

$$E_f = 10^{12} k_d W / (Q_c Q_d M) \quad (2)$$

where

E_f = output stream explosives vapor concentration, pptv;

k_d = dilution-delivery module constant ml²/min-mole; and

Q_d = dilution-delivery module total carrier air flow rate, ml/min.

An examination of equation (1) reveals that variations in FemtoLog explosives vapor output mass flow rate (M_e) are controlled by changing the thermal chamber carrier air stream flow rate (Q_c), and the output concentration is controlled by changing Q_c and/or the dilution-delivery module carrier air stream flow rate (Q_d). For example, a variation of 2 orders of magnitude in M_e and $[E]_f$ can be achieved by varying Q_c from 1 l/min to 0.1 l/min or 10 l/min. Large output variations can also be achieved with small changes to the dilution-delivery module temperature, providing explosives molecules adsorption effects at lower temperatures and thermal decomposition effects at higher temperatures are avoided. At a single operating temperature, only Q_c and Q_d need to be measured during FemtoLog operation, because W is established gravimetrically and k_p and k_d are each a lumped combination of constant operating parameters, dimensions, and configurations of the explosives materials, the thermal chamber, and the dilution-delivery module.

The time required to obtain explosives vapor output equilibrium after changes to Q_c , Q_d , or the dilution-delivery module temperature is approximately 5 to 10 min.

3. System Modules

Traditional dynamic vapor generators comprise three basic modules: a vapor source, a temperature-controlled chamber, and a metered carrier gas stream. FemtoLog adds another module, a dilution-delivery module, downstream of the temperature-controlled chamber. Dynamic vapor generator systems for the common air pollutants have been in use for at least 20 years (Lucero, 1971).

A significant complication arises in generating explosives vapors due to the adsorption characteristics and the low vapor pressure of explosives as stated earlier. Because of these characteristics, explosives vapors have not been generated successfully by permeation devices. Instead, over-the-surface schemes have been used almost exclusively where output rates are determined by sample collection over extended time periods with subsequent analysis and correlation with carrier gas flow rates and other parameters (Pella, 1976; Marshall et al., 1981;

Dionne, 1986).

3.1 PERMEATION BAG

The permeation bag explosives vapor source is a permeation device (Lucero, 1971) that outgasses explosives vapor molecules at a prescribed rate at a given temperature. It is maintained at 75°C to obtain a sufficiently high vapor emission rate such that the average emission rate can be determined gravimetrically with weighings over a 1- to 8-week period for the least volatile explosives such as RDX and PETN.

A large and controlled dilution is obtained with a relatively small carrier air stream. For example, in this application, a 1-l/min carrier air stream flowing over the bag surface will mix with and dilute the RDX concentration from its 7930 pptv equilibrium vapor pressure at 75°C to 5.4 pptv: a factor of 1470. To obtain accurate and constant emission rates to within ± 1 percent, it is necessary only to maintain the bag temperature within $\pm 0.1^\circ\text{C}$ (Lucero, 1971; Williams, 1976; Dionne, 1986).

The primary constraints on the fabrication of an explosives permeation bag are that (1) its tare weight must not exceed 1 g and (2) its operating weight loss must exceed 0.5 μg per week. A permeation bag operating within these specifications allows its emission rate to be determined gravimetrically with commercial microbalances. This operation is obtained by the proper combination of the bag material and dimensions and its equilibrium temperature, as described below.

A typical permeation bag comprises a thin, flat film of Teflon folded over itself, heat-sealed around its edges, and containing explosives material in its interior as depicted by Figure 2. A typical bag containing 0.5 g of pure explosive has an initial tare weight of less than 1 g. For example, a 60-cm² (9.3-in.²) permeation bag of 0.00254-cm (0.001-in.) thick Teflon film will produce an RDX vapor output of 5.3×10^{-11} g/min or 0.53 $\mu\text{g}/\text{week}$ at 75° C. This output is sufficient to produce a 1- μg weight loss over a 14-day period. Thus, an RDX bag operating at 75° C over a 4-week period will provide at least four distinct data points to establish its equilibrium emission rate.

It is noted that the Teflon film itself can experience a weight loss at elevated temperatures (DuPont, undated) due to outgassing of its plasticizers. Only a negligible weight loss is expected at 75°C (DuPont, undated); however, some Teflon permeation tubes have displayed anomalous humps due to plasticizer outgassing in their weight loss rate-time profiles on initial heating to 45°C followed by a steady slightly lower emission rate (Williams, 1976). It appears that the plasticizer outgassing is completed at this temperature because the anomalous hump does not reappear in subsequent weight-time profiles on reheating, and the emission rate attained returns to the previous levels at equilibrium.

Because the bag is in the form of a thin film, it is estimated that the vapor emission rate will reach equilibrium within a few minutes after fabrication. Standard permeation tubes with a 0.762-mm (0.030-in.) thick wall require several days to obtain equilibrium (Lucero, 1971; Williams, 1976). The equilibrium time is essentially the time required to saturate the tube walls or tube material with the vapor molecules. Thus, unlike a permeation tube, changes in temperature of the bag as experienced in removal from the chamber for weighing or transportation and storage, will not affect seriously the utility of the permeation bag, because it can be restored to equilibrium quickly after insertion into a

temperature-controlled bag chamber.¹

Estimated emission characteristics of RDX, PETN, and TNT permeation bags of specified dimensions are listed in Table 1. These estimates are based on a Teflon permeability coefficient of 3.8×10^{-8} std ml/min-cm²-torr/cm for all explosives vapors and on the assumption that the rate-limiting step for the explosives vapor outgassing is the diffusional impedance through the bag membrane wall. The vapor emission rates at 75°C for the bag dimensions shown produce a measurable weight loss ($\sim 1 \mu\text{g}$) in time periods ranging from 1 to 14 days. The RDX permeation bag has the largest dimensions due to its relatively low vapor pressure. Conversely, the TNT bag is the smallest and requires a thicker film as shown because of its relatively high vapor pressure. Note that the output is much higher than the maximum FAA requirement (1 to 5×10^{-15} g), even for a 1-s sampling time by a vapor detection system. Thus, the explosives vapor output from the permeation bag must be attenuated to the desired level. This action is accomplished by the thermal chamber carrier air stream and the dilution-delivery module described later.

3.2 THERMAL CHAMBER

The thermal chamber maintains the permeation bag at a constant elevated temperature ($75^\circ\text{C} \pm 0.1^\circ\text{C}$). It also ensures that the carrier air passage over the bag is in a controlled fashion and subsequently transports the pervaporated vapor molecules to the dilution-delivery module as illustrated by Figure 1. To facilitate the weighing and inspection process, the chamber is equipped with means for convenient access to its interior for permeation bag removal and replacement. For explosives permeation bags, the thermal chamber is also constrained functionally to eliminate or minimize to negligible levels surface adsorption of explosives vapor molecules to the thermal chamber interior walls. Surface adsorption can induce large uncontrolled and unknown explosives vapor concentration variations in the carrier air stream resulting in an unstable vapor generator output. Ordinarily, this constraint is met easily by maintaining the walls at temperature levels at which surface adsorption is minimal, i.e., $> 150^\circ\text{C}$. Because the permeation bag must operate over extended time periods (12 to 30 months) at relatively stable emission rates, this option is not available for this application. The explosives material thermal decomposition rate is unacceptable at 150°C , because it adversely affects the bag emission rate stability as well as its useful life. A 75°C operating temperature level is a reasonable compromise that permits gravimetric determination of the permeation bag

¹Assuming saturation equilibrium is attained after 5 time constants (Lucero, 1969), the time required to obtain emission equilibrium is

$$T = 5 t^2/D = 323.5 \text{ s}$$

where

T = emission equilibrium time, s;

t = bag film thickness, 0.00254 cm; and

D = bag film explosives molecule diffusion coefficient, $1 \times 10^{-7} \text{ cm}^2/\text{s}$.

emission rate and maintains the explosives mass thermal decomposition at a negligible rate for this application.

The chamber thermal control aspects can be addressed by a conventional engineering approach not described. More pertinent to this application are the design features that prevent or at least reduce to negligible levels the adsorption of explosives vapor molecules on the chamber walls. To accomplish this action at 75°C requires a special chamber design as shown in Figure 3. The chamber is basically a concentric tube assembly comprising a solid outer tube and a porous metal inner tube separated by an annular air gap. Heaters and a temperature controller sensor, not shown, are imbedded in the wall of the outer tube.

As carrier gas enters the chamber at 1-l/min, it flows through the adapter and carrier air preheater into the annular space between the cylinders and subsequently through the porous inner tube wall where it emerges at the interior side with a 0.103-cm/s average velocity. This action provides a continuously renewed boundary layer of clean air over the porous surface of the inner tube that explosives vapor molecules do not penetrate, and therefore, they cannot strike and adsorb to the chamber wall (Carter et al., 1978; Mott, undated). For example, the average diffusional velocity or mass transfer coefficient of a TNT or RDX molecule in quiescent or laminar flowing air at 75°C is approximately 0.058 cm/s as determined by the TNT or RDX mass transfer coefficient in the chamber interior. Thus, the net mass transport at the porous wall is in the radial inward direction by a factor of 1.8 relative to the radial outward direction. These estimates are based on a thermal chamber with a cylindrical porous inner wall with a 5.08-cm (2-in.) inside diameter and a 10.16-cm (4-in.) length. At a 1-l/min carrier air flow rate, the net longitudinal flow in the porous cylinder is laminar, and the TNT mass transfer coefficient is 0.058 cm/s, as stated above, for a TNT or RDX in air diffusion coefficient of 0.054 cm²/s.

These mass transport estimates are for worst-case circumstances. For example, not included is the action by the longitudinal carrier gas flow (~ 0.4 cm/s) in the chamber, which reduces the number of explosives vapor molecules that strike the chamber inside wall. The carrier gas promotes an action that sweeps the explosives vapor molecules from the chamber before the molecules strike the chamber wall inside surface (Sanders et al., 1978).

A solid stainless steel tube of 0.635-cm (0.25-in.) diameter, the dilution-delivery module interface tube, protrudes into the porous cylinder at the exit end as shown in Figure 3. It is welded directly to the dilution-delivery module and consequently is near the same temperature (150°C). However, it is not attached mechanically to the porous cylinder, only sealed pneumatically to it by the two O-rings shown. The impact of the hot interface tube (150°C) on the temperature of the thermal chamber (75°C) and porous cylinder is insignificant thermally. Because the temperature of the interface tube is 150°C, a boundary layer is not needed over this surface to prevent vapor adsorption (FAA, 1990).

In review, the entire inner chamber wall with the exception of the interface tube, is provided with a continuously renewed air boundary layer that prevents explosives vapor molecule surface adsorption. In this fashion, the permeation bag can be maintained at 75°C to ensure thermal stability of the explosives vapor as well as explosives material in the permeation bag for an extended period of time and to ensure a stable output rate of explosives vapor molecules from the thermal chamber.

The concentration of explosives vapor molecules in the carrier air stream at the exit of the bag chamber and at the entrance to the dilution-delivery module is

$$[E]_c = (V_m W / MQ_c) 10^{12} \quad (3)$$

where

$[E]_c$ = chamber carrier air stream explosives molecule concentration, pptv; and

V_m = molar gas volume, 24,000 ml/mole at 20°C.

3.3 DILUTION-DELIVERY MODULE

It is also noted from Table 1 that vapor emission rate levels are above those required for an explosives vapor detection system evaluation and calibration. Thus, additional operations are performed on the thermal chamber carrier air stream to attenuate the explosives vapor output rate. The dilution-delivery module of Figure 4 accomplishes this reduction over several orders of magnitude in a precise and controlled fashion and a over a range of transport air flow rates. These features also extend the vapor generator utility for simulation of a large number of detection scenarios.

FemtoLog is operated in a manner such that an identical explosives vapor mass output rate is generated regardless of the dilution-delivery module air stream flow rate; only the explosives vapor concentration changes. It is presumed that the user will establish the output gas flow rate to interface with a specific vapor detection system and, therefore, set the air flow rate to the appropriate level. The dilution-delivery module uses a heated, tubular, semi-permeable membrane to extract a small fraction of explosives vapor molecules from the thermal chamber carrier air stream by diffusion through the tube wall.²

For example, a 1.8×10^{-12} ml/min chamber stream of RDX molecules is extracted from the carrier stream shown in Table 1. The tube is a 1.75-cm (0.75-in.) diameter cylinder, 25-cm (10-in.) long. It is maintained at 150°C by the air preheater and the heater and temperature control sensor attached to the chamber walls which enclose the tube. Two

²The flow rate of explosives vapor molecules radially outward through a tube is (Lucero, 1976)

$$Q_e = 2 \pi L P_m p / \ln (r_o / r_i) = 0.185 \times 10^{-12} \text{ std ml/min}$$

where

Q_e = explosives vapor permeation flow rate through the tube wall, std ml/min;

L = tube length, 25 cm;

P_m = tube material explosives vapor permeability coefficient, 8×10^{-7} std ml/min-cm²-torr/cm for RDX through Teflon at 150° C;

p = RDX partial pressure of the carrier air stream, 4.08×10^{-9} torr (see Table 1);

r_o = tube outside radius, 0.318 cm; and

r_i = tube inside radius, 0.241, cm.

bulkhead fittings penetrate the inlet end of the tube chamber. One fitting allows the thermal chamber carrier air stream carrying explosives vapor molecules to enter through 0.635-cm stainless steel tubing and flow through the core of the tubular membrane, while the second fitting permits the dilution-delivery module air to enter the chamber at approximately 1 l/min and sweep away the explosives vapor molecules diffusing through the tubular membrane wall into the annular space and subsequently to the fluidic switching chamber. A cylindrical lattice suspends and supports the tubular membrane. The thermal chamber carrier air stream flows out of the dilution-delivery module through an exit bulkhead fitting to an explosives vapor scrubber cartridge and is vented to the room.

The heated fluidic valve assembly of Figure 4 diverts the dilution-delivery air stream to the scrubber and out of the system or to the ambient air or into a detection system. In the FemtoLog standby condition, the valve diverts the dilution-delivery air stream to the scrubber, or to the detection system in a continuous or pulsed fashion.

The explosives vapor concentration of the FemtoLog output stream is

$$E_f = 2 \omega L P_t V_m P_m W 10^{12}/M Q_c Q_d \ln (r_o/r_i) \quad (4)$$

where

E_f = output stream explosives vapor concentration, pptv;

L = extractor tubular membrane length, cm;

P_t = total absolute gas pressure in the extractor (atmospheric pressure), torr;

P_m = tubular membrane material permeability coefficient at 150°C, ml/min-cm²-torr/cm;

r_o = tubular membrane outside radius, cm; and

r_i = tubular membrane inside radius, cm.

The dimensional, configuration, and material properties of the tubular membrane of equation (4) are lumped into the dilution-delivery module constant (k_d):

$$k_d = 2 \omega L P_t V_m P_m / \ln (r_o/r_i) \quad (5)$$

Note that to obtain the FemtoLog explosives vapor output concentration, measurements of Q_c and Q_d are required.

The explosives vapor mass flow rate in the mixture tube or the FemtoLog output stream is $M_e = Q_e W_e$:

$$M_e = [2 \omega L P_m V_m P_t / \ln (r_o/r_i)] [W_e/MQ_c] \quad (6)$$

where

Q_e = explosives vapor molecule extraction rate by the dilution-delivery module, ml/min; and

W_e = explosives vapor density, g/ml.

As described by equation (6), the FemtoLog mass constant, (k_p), is $k_p = k_d W_e$.

Note that to obtain the FemtoLog explosives vapor mass output flow rate, only a measurement of Q_c is required.

4. Design Considerations

Most of the FemtoLog unique design features, constraints, and specifications arise from or are associated with the special performance requirements of the first dilution stage, i.e., the permeation bag and thermal chamber.

Conceptually, the permeation bag is a relatively simple device to fabricate and operate. However, experience logged by the authors suggests strongly that all direct manipulations with the bag must proceed carefully and deliberately over the entire bag life from fabrication to disposal. It is essential to examine and inspect the Teflon film and the permeation bag for the absence of plasticizer outgassing and seam and pinhole vapor leaks. Special handling procedures must be formulated and tools and fixtures developed and used to (1) suspend the permeation bag in the thermal chamber and (2) perform the gravimetric determinations without contaminating the thermal chamber walls and the analytical balance with explosives or cross-contaminating the bags, thus avoiding spurious results from water vapor adsorption. The importance of these items was discussed only briefly above, yet nonetheless, they are paramount to successful operations.

Novel design considerations of the thermal chamber center on the pneumatic and mechanical aspects associated with the inner porous cylinder. Formation of an adequate, continuously renewed air boundary layer is functionally dependent on a parametric combination of carrier gas flow rate and the cylinder pore size, porosity, and dimensions at the operating temperature level. Thus, the 1-l/min carrier gas flow rate specified above was primarily for discussion purposes. The actual flow rate, although probably near 1-l/min, is determined only after the porous cylinder characteristics are fixed, the method of flow rate control is selected, and the source of carrier air is defined. For example, a relatively high pressure (~ 1 MPa) carrier air source permits the use of a critical orifice for flow rate control and a cylinder with a large pressure drop. All other aspects of the chamber including easy and convenient access/egress ports for the permeation bag are determined by fundamental engineering approaches.

Similar conclusions apply to the dilution-delivery module design. In this case, it is prudent to consider the dilution-delivery module internal dimensions affecting the air stream flow rate to obtain a reasonable flow rate level as constrained by the tube stream pressure drops and total pressure head available. In this same regard, it is important to be apprised of the limits of a pressure-flow rate trade-off for the dilution-delivery module air stream.

5. Operation

There are two basic FemtoLog operating constraints: the generator-detection system interface and the generator standby operation.

The interface configuration and conditions are best defined quantitatively and specifically in conjunction with the calibration and operational requirements of specific

detection systems. Certainly, the generator total explosives mass output per calibration episode, i.e., mass for a single examination, is established by a typical worst-case scenario defined by the user. However, the generator explosives vapor concentration output and air output flow rate is constrained to an extent by the detection system sample ingestion flow rate and sampling time period. Secondary interface considerations are defined by the detection system sampling procedure and process. These interface considerations may be regarded as special-purpose interface constraints associated with a specific type or class of detection system. For the range of detection system operating conditions anticipated, adjustments to the FemtoLog flow rates and the bell-mouth exit area can be implemented without affecting its performance specifications.

All vapor generators using permeation type sources require special standby operational considerations. These arise because the vapor emission from a permeation device continues despite its operating mode, i.e., standby or calibration (Lucero, 1971). Also, the thermal chamber carrier gas flow rate must be maintained in the standby mode. Thus, FemtoLog is functionally always in the operating mode unless special provisions are included for standby, e.g., removal, storage, and reinstallation of the permeation bag. Perhaps the calibration/standby question is relatively unimportant for a strictly laboratory application. For a field unit, the power and expendables consumed in supplying air to the vapor generator and most likely the transportability and the unwanted acoustical noise radiating from pumps or blowers and the air jets can be serious nuisances. Certainly, these items are a disadvantage of permeation vapor generating systems. The overall impact of this operational issue has been assessed. The authors, however, defer in expanding on this issue until the calibration duty time fraction is better established or an automated operation for standby-to- calibration-to-standby change is deemed desirable from a value engineering analysis perspective.

It is probable that it may be necessary to develop special weighing procedures and fixtures to perform more accurate and precise gravimetric determinations if required. Experience has shown that emission rate determinations display maximum variations of ± 15 percent over a 6-month period. This apparent instability is ascribed mainly to ambient air water vapor adsorption to the permeation bag outside surface during the weighing period, i.e., immediately after its removal from the thermal chamber and the end of the weighing process by the analytical balance. Thus, the primary function of special procedures and fixtures is to eliminate or minimize to negligible levels water vapor adsorption to the permeation bag outside surface.

FemtoLog can be controlled and adjusted from the front panel. The explosives vapor mass flow rate and concentration output as well as the total gas flow rate output is controlled and adjusted by varying the thermal chamber carrier air stream flow rate (Q_C) and/or the dilution-delivery module total carrier air flow rate (Q_D). The minimum requirements for controlled manipulation of the parameters are front panel or other output measurements of Q_C and Q_D and corresponding flow rate adjustment devices, e.g., valves, regulators, flow controllers. All other output are primarily status indicators, e.g., thermal chamber and dilution-delivery module temperature.

6. Acknowledgements

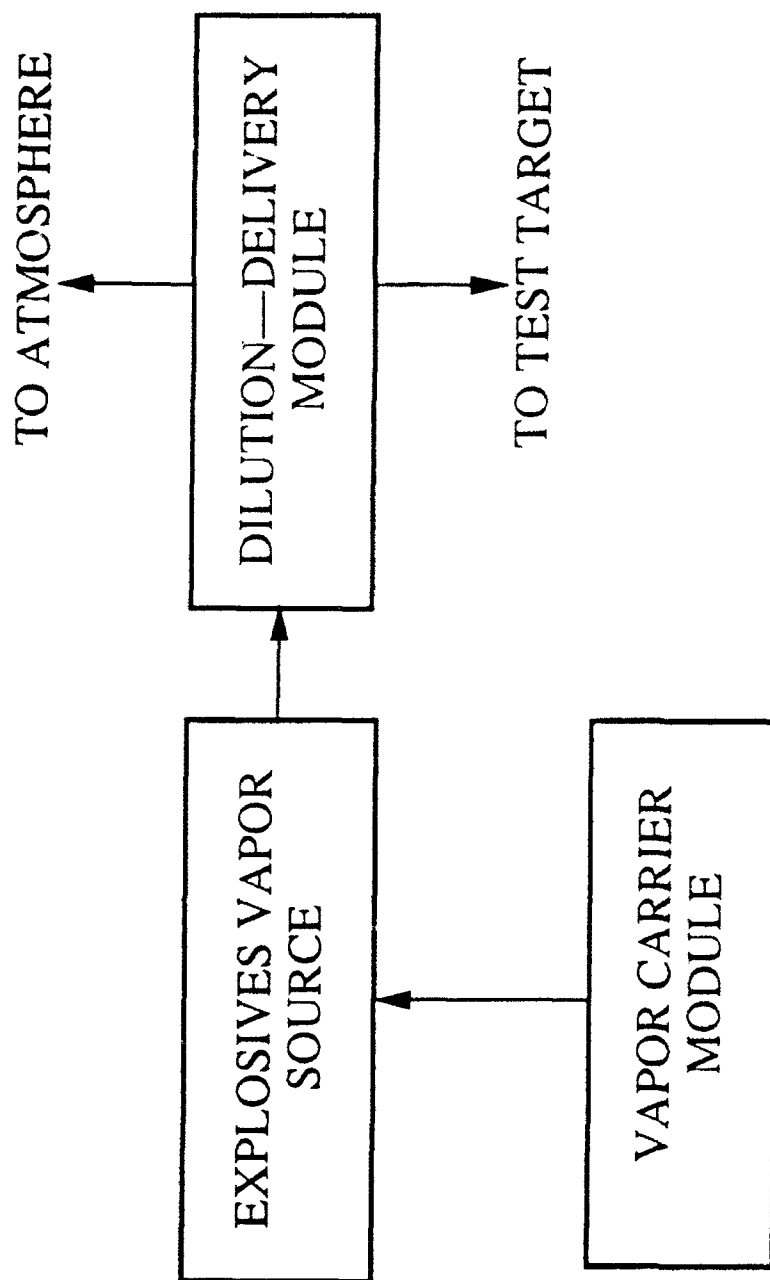
The authors acknowledge the contributions of Jason P. Merkoski of the Massachusetts Institute of Technology in Cambridge, Massachusetts, USA for the editorial and graphics work and S. K. Hendrikson of E-Cubed, Inc. of Germantown, Maryland, USA for design assistance and conception of the permeation bag.

7. References

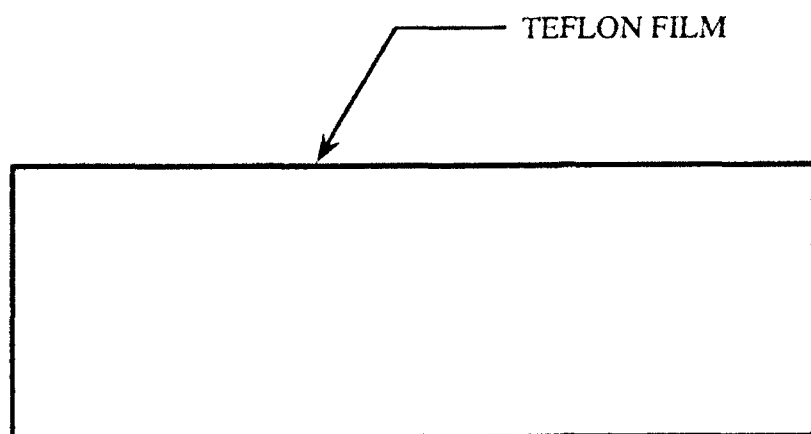
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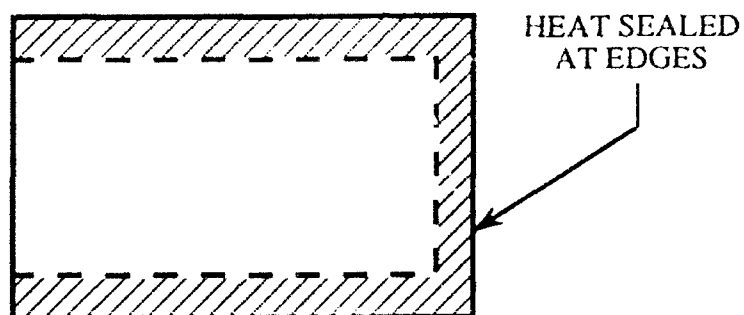
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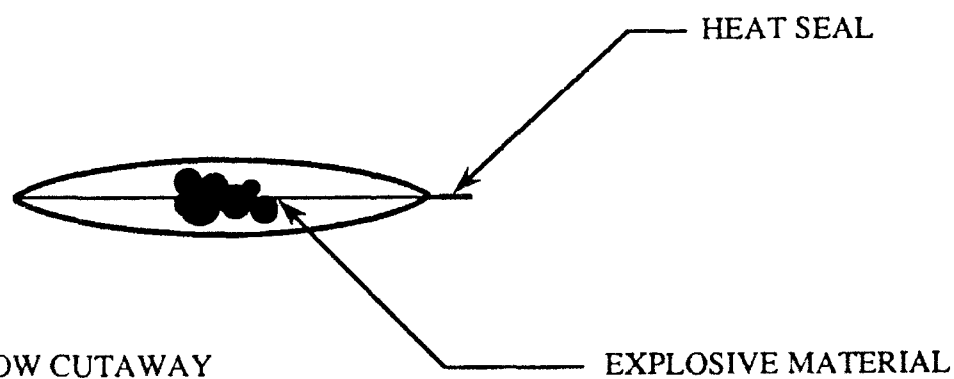
**FIGURE 1 — FEMTOLOG (EXPLOSIVES VAPOR GENERATOR)
PNEUMATIC NETWORK**



(A) PILLOW FLAT PATTERN



(B) SEALED PILLOW



(C) PILLOW CUTAWAY

FIGURE 2 — PERMEATION BAG

TABLE 1. Permeation Bag Characteristics

Operating Conditions: Bag Temperature $\sim 75^{\circ}\text{C}$
 Permeability Coefficient $\sim 3.8 \times 10^{-8}$ std ml/min-cm²-torr/cm (estimated)
 Bag Material — Teflon
 Carrier Gas Flow Rate ~ 1 l/min

Vapor Species	Concentration ^a (ppt)	Thickness (cm)	Area (cm ²)	std ml/min	Emission Rate ^b $\mu\text{g/day}$	pg/s
RDX	7,930	0.00254	5.95	5.37×10^{-9}	0.077	0.895
PETN	55,819	0.00254	6.02	3.82×10^{-9}	0.078	0.898
TNT	4,170,000	0.00762	4.20	6.64×10^{-8}	0.97	11.3

^a Dionne et al., 1986

^b $Q_e = 7.6 \times 10^{10} A P_m P_e / t$

where

Q_e = Explosives molecule permeation rate from bag, std ml/min

A = Bag cross-sectional permeation area, cm²

P_m = Bag film material explosives vapor permeability coefficient, std ml/min-cm²-torr/cm

P_e = Explosives equilibrium vapor pressure at bag temperature, pptv

t = Bag average film thickness, cm

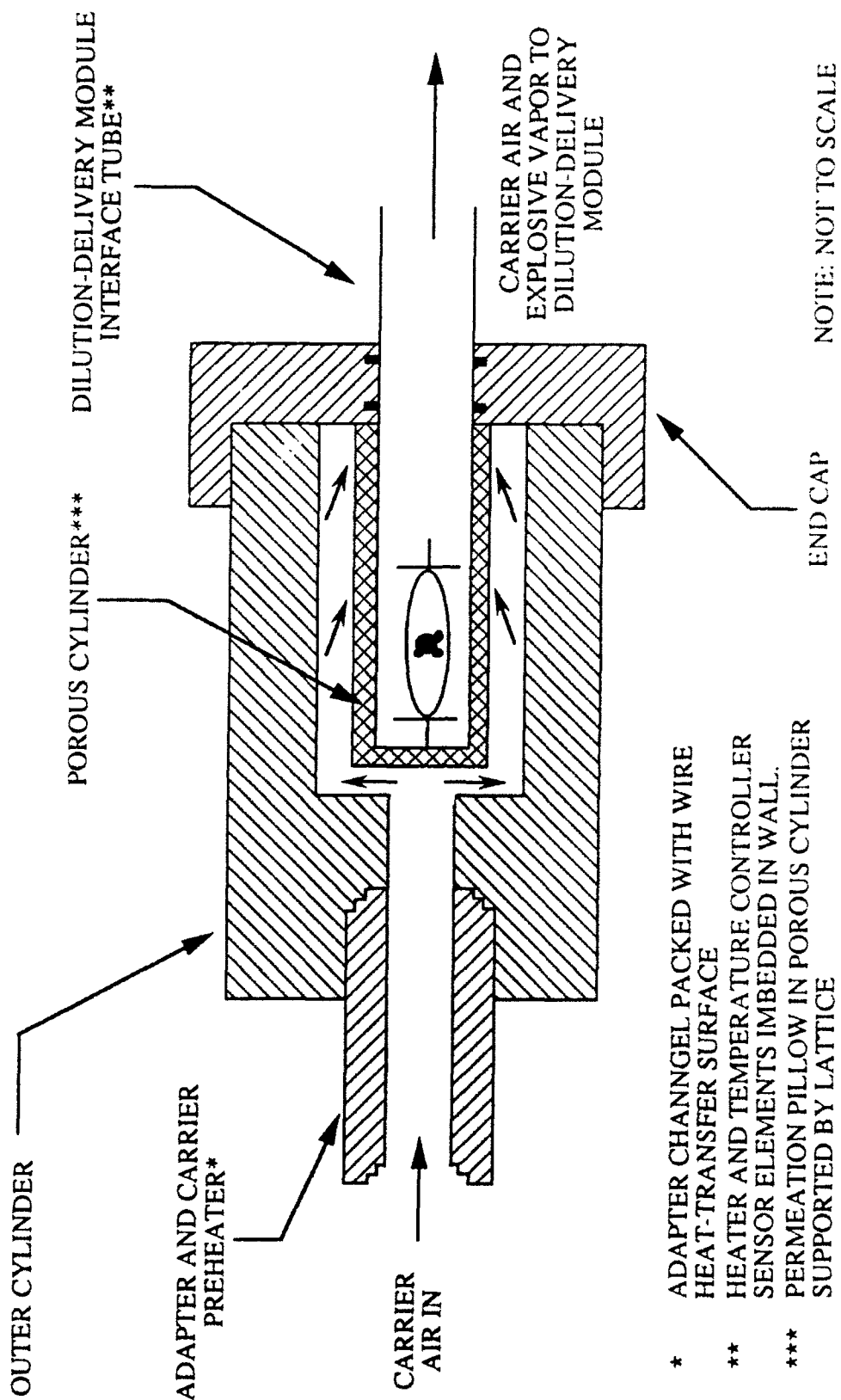


FIGURE 3 — PERMEATION PILLOW THERMAL CHAMBER

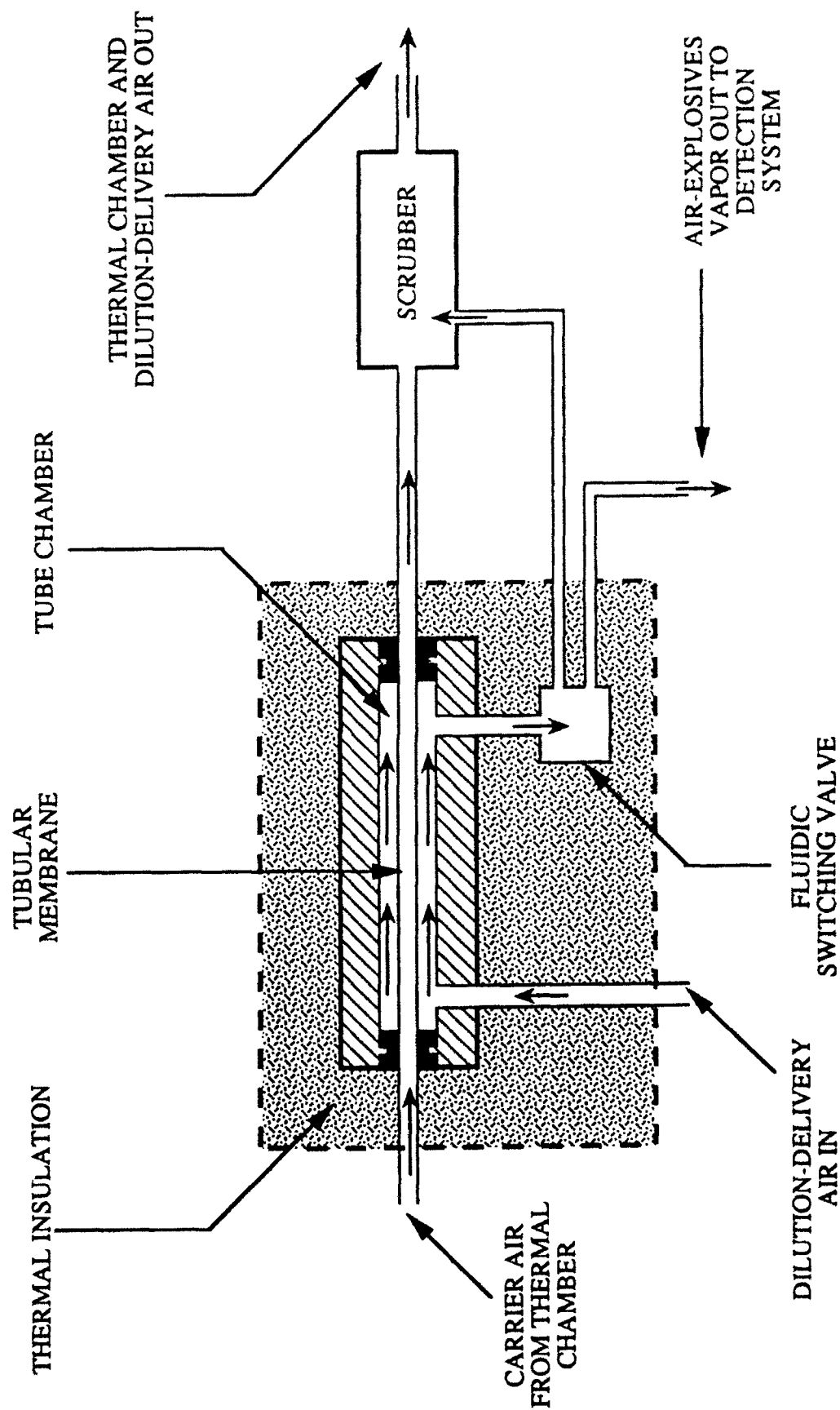


FIGURE 4 — DILUTION-DELIVERY MODULE

A MODEL OF EXPLOSIVE VAPOR CONCENTRATION II

Thomas A. Griffy
Physics Department
University of Texas
Austin, Texas 78712
USA

ABSTRACT. A theoretical model which predicts the expected concentration of explosive vapor which might be available for detection in various scenarios was reported at a previous conference (Mannheim 1989). The results of this model have now been refined and the model extended to apply to other situations. A comparison has been made of the predictions of this model with experimental results obtained in a controlled experiment in a room-sized environment. The experimental results are found to be in good agreement with the theoretical predictions.

1. Introduction

In a previous communication¹ a model which describes the time dependance of the concentration of explosive vapor in an enclosed space was presented. The most important, and somewhat surprising, result of this model is that the vapor pressure of the explosive in this space remains many orders of magnitude below the equilibrium vapor pressure of the explosive for a substantial time (many days) following the insertion of the explosive. Thus using vapor detectors ("sniffers") is a far more difficult task than one would anticipate if the sensitivity required is estimated using equilibrium vapor pressures.

In the present paper the previous results are reviewed, the model is extended to predict the amount of explosive likely to be found on the surfaces of the enclosed space and the predictions of the model are compared with some experimental results.

2. Summary of previous results

If a quantity of explosive is placed in an enclosed space (the "room") the vapor pressure

of the explosive does not immediately assume its equilibrium value p_* . The actual vapor pressure p at a given time is determined by three competing processes: the rate of evaporation of explosive, the rate at which the explosive strikes and sticks to the various surfaces in the room, and the rate of air exchange in the room produced by the ventilation system. Thus the time rate of exchange of the vapor pressure is given by

$$\frac{dp}{dt} = \alpha (p_* - p) - \beta p - \gamma p$$

where the first term on the RHS describes evaporation, the second term loss to the walls, and the third term air exchange. Once the three rate constants of α , β , and γ are determined, the equation can be integrated to obtain the vapor pressure of p as a function of time:

$$p(t) = \frac{\alpha}{\alpha + \beta + \gamma} p_* (1 - \exp(-(\alpha + \beta + \gamma)t))$$

In the previous paper some rather simplistic arguments were used to estimate the values of α and β . (γ is simply the reciprocal of the time required for one air exchange in the room.) These simple arguments led to the result that, until all the surfaces in the room become coated with explosive, the vapor pressure is lower than the equilibrium pressure by a factor of A_E/A_S where A_E is the surface area of the explosive and A_S is the surface area of all the surfaces in the room (walls, ceilings, windows, etc.). For a one-pound block of explosive in a typical room $A_E/A_S \sim 10^{-4}$ indicating that the vapor pressure would be four orders of magnitude less than the equilibrium value.

3. Extensions of the model

To obtain a better estimate of the evaporation rate constant α we assume the explosive evaporating from the surface of the explosive is trapped in a thin boundary layer at the surface of the explosive and very quickly reaches its equilibrium concentration C_* (kg/m^3) in this small volume. The vapor then reaches the room by diffusing through this boundary layer. This process results in a mass flux which is given by

$$J = C_s \frac{D}{\bar{\delta}}$$

where J is the mass flux ($\text{kg/m}^2\text{s}$), D is the diffusion coefficient for the explosive in air (m^2/s) and $\bar{\delta}$ is the average boundary layer thickness (m). The equilibrium concentration is related to the vapor pressure by the gas law,

$$C_s = \frac{Mp_s}{RT}$$

where M is the molecular weight (kg/mole), R is the gas constant (8.31 J/mole K) and T is the temperature (K). The diffusion coefficient can be estimated from the formula for rigid elastic spheres

$$D_{12} = \frac{3}{8(n_1 + n_2) \sigma^2} \left(\frac{kT (m_1 + m_2)}{2\pi m_1 m_2} \right)^{1/2}$$

where n is the molecular density of the two gases, m the mass of the molecule, σ the effective collision diameter and k is Boltzmann's constant ($1.38 \cdot 10^{-23} \text{ J/K}$).

The average boundary layer thickness can be estimated from the formula²

$$\bar{\delta} = \frac{5}{2} \left(\frac{l\mu}{\rho U_s} \right)^{1/2}$$

where l is the characteristic length of the boundary, μ is the viscosity of air ($18 \cdot 10^{-6} \text{ Pa}\cdot\text{s}$), ρ is the density of air ($1.29 \cdot \text{kg/m}^3$) and U_s is the velocity of the air over the surface.

Using the ideal gas law once again, the evaporation rate constant α becomes

$$\alpha = \frac{DA_E}{V\bar{\delta}}$$

where V is the volume of the room.

These results for the evaporation rate J and the rate constant α will be compared to experimental results in the next section.

The remaining rate constant to be determined is the rate at which explosive is lost by striking and sticking to the various surfaces in the room. The kinetic theory of gases provides a formula for the mass flux striking the surfaces³

$$j = \left(\frac{M}{\pi RT} \right)^{1/2} p$$

where p is the explosive vapor pressure. Let σ (kg/m^2) be the amount of explosive per unit area found on the surfaces and σ_* the saturation value of this parameter. If one assumes the probability of sticking in a given collision is v then the mass flux to the walls is given by

$$\frac{d\sigma}{dt} = vj \left(1 - \frac{\sigma}{\sigma_*} \right).$$

The rate constant β satisfies a similar equation

$$\beta = \beta_* \left(1 - \frac{\sigma}{\sigma_*} \right)$$

where β_* is the value of β at the time $t = 0$,

$$\beta_* = v \left(\frac{RT}{2\pi M} \right)^{1/2} \frac{A_S}{V}.$$

Taking the time derivative of the equation for β

$$\frac{d\beta}{dt} = - \frac{\beta_*}{\sigma_*} \frac{d\sigma}{dt} = - \frac{\beta_*}{\sigma_*} vj \left(1 - \frac{\sigma}{\sigma_*} \right)$$

$$= -v \frac{p_0}{\sigma_0} \left(\frac{M}{2\pi RT} \right)^{1/2} \frac{p}{p_0} \beta.$$

One can now use the approximate solution for p given in section 2

$$p = \frac{\alpha}{\alpha + \beta + \gamma} p_0.$$

to obtain, after some algebra, the following transcendental equation for β :

$$\epsilon \ln \frac{\beta}{\beta_0} + \frac{\beta}{\beta_0} - 1 + \frac{t}{\tau} = 0$$

In writing this equation we have introduced a time τ , which is the time required to coat all of the surfaces to saturation if all of the explosive evaporating from the block was immediately used to coat these surfaces.

$$\tau = \frac{\sigma_0 A_S}{J A_E}$$

We have also introduced a dimensionless parameter ϵ which is also given by

$$\frac{1}{\epsilon} = \frac{v A_S}{V} \left(\frac{RT}{2\pi M} \right)^{1/2} \frac{1}{\alpha + \gamma}$$

If ϵ is small, which is usually the case in most situations, then the logarithmic term in the equation for β can be neglected and one obtains simply

$$\beta = \beta_0 \left(1 - \frac{t}{\tau} \right) \quad \text{for } t \leq \tau$$

$$\beta = 0 \quad \text{for } t > \tau$$

The amount of explosives found on the surfaces in the room is then given by

$$\sigma = \sigma_s \frac{t}{\tau} \quad \text{for } t \leq \tau$$

$$\sigma = \sigma_s \quad \text{for } t > \tau$$

For those cases where ϵ is not small a table of β/β_s as a function of t/τ is given in the appendix.

Once $\beta(t)$ is determined, either from the equation above valid for the small ϵ or from the appendix, the vapor pressure can then be obtained from the equation

$$p(t) = \frac{\alpha}{\alpha + \beta(t) + \gamma} p_s.$$

Two important results follow immediately from this equation. First, for times t small compared with τ , $p \ll p_s$ since $\beta \gg \alpha$. Second, even following saturation of all of the absorbing surfaces ($\beta = 0$) p is still less than p_s since $\alpha/(\alpha + \gamma) < 1$. This last is simply the effect of air exchange on the vapor pressure.

4. Numerical Results and Comparison with Experiments

In order to illustrate the usefulness of the equations developed in section 3, we will use these results to calculate some of the properties of TNT vapor. The equilibrium vapor pressure of TNT was taken to be $9.4 \cdot 10^{-4}$ Pa and the diffusion coefficient was estimated to be $1.0 \cdot 10^{-5}$ m²/s. Using the values of $1.8 \cdot 10^{-5}$ Pa · s as the viscosity of air and 1.29 kg/m³ as the density of air, the evaporation rate of TNT is predicted to be

$$J = 9.6 \cdot 10^{-11} \left[\frac{U_s}{l} \right]^{1/2} \text{ kg/m}^2 \cdot \text{s}$$

where U_s is the airstream velocity across the surface of the explosive and l is a characteristic length associated with this surface.

The evaporation rate from a small sample of TNT ($l = .03$ m) has been measured as a function of the airstream velocity (B. Dennis, private communication). These results are

shown in figure 1. The predicted evaporation rate, shown as a solid line in the figure, agrees quite well with the experimental values.

As a further check on the predictions of this model a small sample of TNT (surface area $A_E = 0.01\text{m}^2$) was placed in a room (dimensions $2.9\text{m} \times 2.9\text{m} \times 2.11\text{m}$) and the vapor pressure of the explosive in the room and the amount of explosive found on the walls of the room were measured as a function of time. Using the room dimensions and a measured air exchange rate of once per hour, the characteristic time τ turns out to be $4.3 \cdot 10^7\text{s}$ (500 days). Samples were taken to determine the amount of TNT found on the walls after 80 days. The average from several samples was $1.3 \cdot 10^{-7}\text{ kg/m}^2$. Assuming a saturation value σ , of 10^{-6} kg/m^2 (a monolayer of TNT), the model predicts the amount found on the walls should be $1.5 \cdot 10^{-7}\text{ kg/m}^2$ in reasonable agreement with the experimental result.

The amount of TNT vapor found in the room after 80 days was $3.5 \cdot 10^{-5}$ times the equilibrium vapor pressure. Although the model predicts a significant reduction of the vapor pressure compared to the equilibrium value, indeed this is the most important result of the model, the exact value depends on the unknown parameter v which is the probability that an explosive molecule will "stick" to the walls each time it strikes them. The experimental results agree with the model if one uses a sticking probability of $2 \cdot 10^{-4}$, a not unreasonable value.

Summary and Conclusions

A previously proposed model for the time dependence of explosive vapor concentration has been extended and the predictions of the model compared with two experiments. *The main prediction of this model is that the vapor pressure of the explosive is many orders of magnitude less than the equilibrium vapor pressure. The practical implication of this result is that explosive detectors which function by collecting air samples are unlikely to be effective unless their sensitivity is orders of magnitude greater than that required to detect equilibrium amounts of the vapor.*

The predictions of the model have been compared with two experiments on the rate of evaporation of TNT and the amount of TNT vapor found in an average size room. The model agrees reasonably well with these experiments.

Appendix

Solutions to the equation

$$\varepsilon \ln \frac{\beta}{\beta_0} + \frac{\beta}{\beta_0} - 1 + \frac{t}{\tau} = 0$$

$\frac{t}{\tau}$	$\frac{\beta}{\beta_0}$				
	$\varepsilon = 10$	$\varepsilon = 1$	$\varepsilon = 0.1$	$\varepsilon = 0.01$	$\varepsilon = 0.001$
0.2	0.982	0.903	0.820	0.802	0.800
0.4	0.956	0.811	0.644	0.605	0.601
0.6	0.947	0.725	0.475	0.409	0.401
0.8	0.930	0.644	0.316	0.216	0.201
1.0	0.914	0.569	0.176	0.034	0.005
1.2	0.897	0.500	0.069	-	-
1.4	0.881	0.437	0.016	-	-
1.6	0.865	0.379	0.003	-	-
1.8	0.849	0.327	-	-	-
2.0	0.834	0.281	-	-	-
5.0	0.632	0.019	-	-	-
10.0	0.394	-	-	-	-
20.0	0.150	-	-	-	-

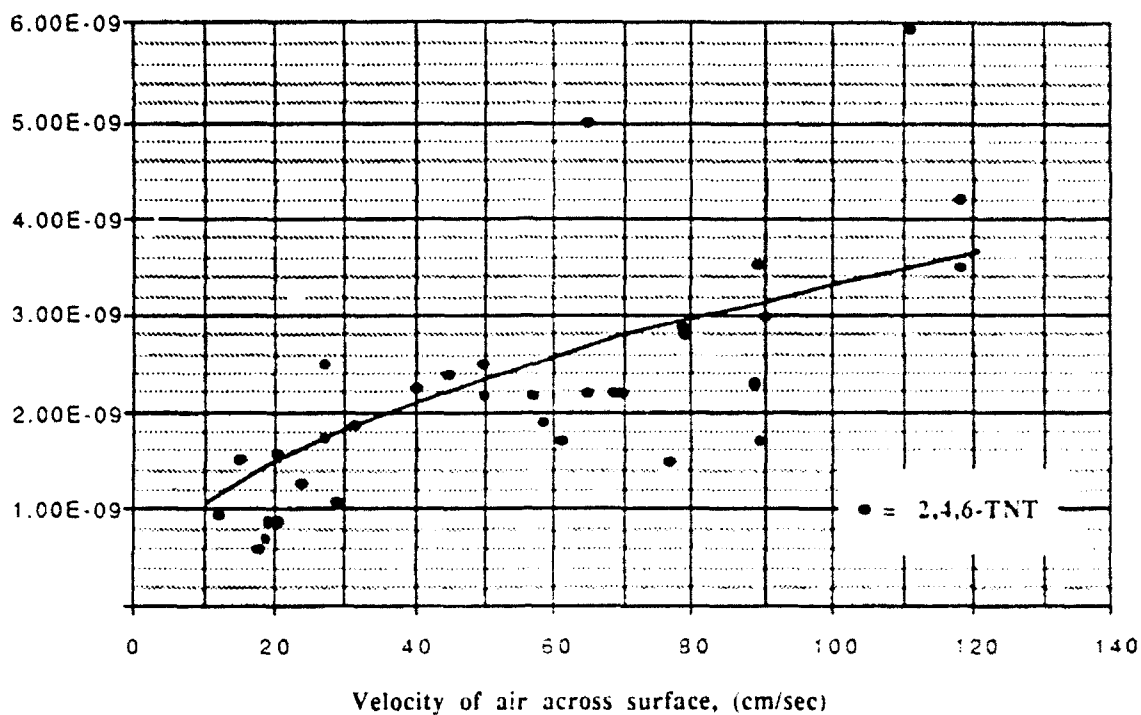


Figure 1. Plot of the rate of evaporation of TNT as a function of the velocity of nitrogen across the surface.

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- ¹ T.A. Griffy, Proceedings of the Third Symposium of Analysis and Detection of Explosives, Mannheim Germany, 1989.
 - ² E.U. Condon and H. Odishaw, "Handbook of Physics", Second Edition, McGraw-Hill, New York, 1967, p. 3-29.
 - ³ M.W. Zemansky, "Heat and Thermodynamics", McGraw-Hill, New York, 1968, p.164.

DESIGN AND CALIBRATION OF PULSED VAPOR GENERATORS FOR TNT, RDX AND PETN

J. P. Davies, L. G. Blackwood, S. G. Davis, L. D. Goodrich
and R. A. Larson
Idaho National Engineering Laboratory
P. O. Box 1625
Idaho Falls, ID, 83415
United States of America

ABSTRACT. Computer controlled explosive vapor generators for 2,4,6-trinitrotoluene (TNT), cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX) and pentaerythritol tetranitrate (PETN) were built and calibrated to support an Independent Validation and Verification (IV&V) facility for Explosive Detection Systems (EDS) for the Federal Aviation Administration (FAA) at the Idaho National Engineering Laboratory. The generators were constructed using pure explosive suspended on quartz beads which were then loaded into a stainless steel tube. The tube was coiled and placed into a temperature controlled chamber. A carrier gas (ultra-pure air) was passed through the coil to carry the explosive molecules. The generators are capable of delivering a pulse of varying explosive mass through the control of coil temperature, air flow rate, and pulse width. Preliminary calibrations have been completed in the picogram to nanogram range using an Ion Mobility Spectrometer (IMS) as the calibrating instrument. The explosive vapor generators will be used as quantitative vapor standards to establish the lower limit of detection for EDS systems at the IV&V.

INTRODUCTION

Over the last 15 years explosive vapor generators have been constructed by a number of investigators. The first generators were of a basic design that included the explosive in a temperature controlled reservoir through which a carrier gas is passed to carry the explosive vapors. These include designs by Pella¹, Krzymien et al.², Carter et al.³ and Hobbs et al.⁴. All of the above generators are continuous flow systems.

The generators needed in the IV&V tests are required to deliver a pulse of explosive vapors between 1 and 1,000 picograms in less than 5 seconds with a high degree of accuracy. The mass output will be varied during a test with only a few minutes between pulses. Pulsed systems have been reported by Reiner et al.⁵ and McGann et al.⁶. Reiner's system uses a modified gas chromatograph (GC). An aliquot of

a standard is injected into the GC resulting in the emission of the vaporized explosive at the exit of the capillary column. The system by McGann uses a heated syringe which contains a reservoir of the explosive in the syringe barrel. The difficulty in preparing standards at the low pg level and the significant variability in the output from the GC generator⁵ and the lack of controls in the syringe method led us to construct a new pulsed vapor generator. The system is based on the design of Carter et al⁵.

In this paper the design and preliminary calibration of the explosive vapor generators will be discussed. An Ion Mobility Spectrometer (IMS) was used to calibrate the generators mass output. The calibration of the IMS will also be discussed.

EXPERIMENTAL

VAPOR GENERATOR CONSTRUCTION

A diagram of the vapor generator system is presented in Figure 1. The system is composed of four parts, a thermostated explosive vapor reservoir, a flow control manifold, a supply of thermostated air and a computer data acquisition/control system (not shown on the schematic).

Explosive reservoir. The explosive reservoir contains approximately 0.1 grams of solid explosive suspended on quartz beads. The explosive, either TNT, RDX or PETN, is dissolved in ~15 ml of methyl ethyl ketone. Between 20 and 22 g of 0.1 mm diameter quartz beads are added to the solution. The mixture is stirred during solvent evaporation to aid in homogeneous deposition of the explosive on the beads. The explosive coated beads are then loaded into a cleaned 10 foot long thin walled 1/8 inch OD stainless steel tube. A 1/2 inch long plug of quartz wool is packed into both ends of the tubing to hold the beads in place. In the case of the TNT and PETN tubes, 1/2 inch of empty tubing remains at both ends. The RDX coil is constructed with 1 foot of empty tubing at both ends (The reason for the latter tube design is discussed in the results section). After packing, the tubing is coiled around a 2" thin-walled aluminum tube and placed inside of a 3" thin walled outer aluminum tube with aluminum end caps. The temperature of the explosive reservoir is controlled to within $\pm 0.1^\circ\text{C}$ by varying the flow rate of the heating/cooling air through the aluminum canister. The explosives reservoir temperature is monitored by two thermocouples. The thermocouples are positioned 2 1/2 inches from each end of the coil in the TNT and PETN generators and 1 foot from each end of the coil in the RDX generator. A nicrome wire heater maintains the last inch of the vapor generator coil at $4 \pm 1^\circ\text{C}$ higher than the rest of the generator to eliminate deposition of explosive vapors at the outlet. This last region is monitored by a third thermocouple positioned 1/2 inch from the outlet.

Flow control manifold. The carrier gas flow rate is set using a micrometer needle valve (V-1). During the initial setup and between

explosive vapor pulses, the carrier gas is diverted using a three way solenoid valve (SV-1) to the setup manifold. The setup manifold is used to simulate the resistance of the generator by adjusting a needle valve (V-2) at the end of the manifold. The resistance adjustment is optimized by monitoring the differential pressure vs time (dPt) response across the generator coil during a pulse of air flow through the generator. A 0-3.6 psig differential pressure cell (Pt-2) is used to monitor the above. When the resistances of the coil and the setup manifold match, the leading edge of the dPt response will rise and level off rapidly. A resistance mismatch will result in either overshooting the final differential pressure (too large of manifold resistance) or a gradual rise to the final differential pressure value (too small of a manifold resistance). An additional pressure transducer (PT-3) is present in the manifold to check the system for leaks.

Data Acquisition/Control System (DACS). The DACS is used to monitor and control various parameters of the vapor generator. The DACS consists of an IBM PS/2 personal computer that utilizes National Instruments MC-MIO-16(L/H)-25 multi-function input/output data acquisition board.

The DACS monitors all 3 thermocouples in the vapor generator, the carrier gas flow rate and the pulse integral (dPt). Explosive vapor pulses are set and controlled on the DACS. During a pulse the carrier gas is switched from the setup side of the vapor generator system to the vapor generator coil via the three-way solenoid valve (valve SV-1). When the injection is completed the flow is switched back to the setup side of the system and a 2-way solenoid valve (SV-2) is opened to relieve the back pressure in the vapor generator line to reduce trailing of the explosive vapor out the generator. The output of the generator is monitored using the change in the dPt across the coil because the response of the flowmeters is too slow to be used. During a typical calibration the flow rate is changed over the range of 20 to 100 ccm and the variability in the dPt over this range is less than $\pm 1\%$.

VAPOR COLLECTION TUBES

A preconcentrator is used to collect explosive vapors from the vapor generator for subsequent quantification. These preconcentrators are also used to inject standards into the IMS. A preconcentrator consists of a 3.8 mm long X 5.7 mm OD X 4.0 mm ID quartz glass tube (Richland Glass Co.) containing 5.0 ± 1.0 mg of quartz wool packed into a 13 mm plug positioned 13 mm from the front end of the tube. D. W. Hannum⁷ at Sandia National Laboratories has characterized similar preconcentrators with respect to the collection and release of explosive vapors. Hannum reported a quantitative release of adsorbed explosives and a collection efficiency of $\sim 100\%$.

MATERIALS

Quartz tubing is cleaned with methanol then baked at 225°C. Quartz wool in the preconcentrators is baked after the preconcentrator is assembled at 225°C. All stainless steel tubing is first rinsed with acetone then methanol. The tubing is then baked at 300°C with a nitrogen purge. All teflon tubing is baked at 100°C with a nitrogen purge. Refrigerator grade copper tubing for the heating and cooling air is used as received. Swagelok brand fittings connecting the stainless steel as well as the teflon tubing are stainless steel and pre-cleaned in acetone followed by methanol followed by baking at 225°C.

Solvents are used as received. Methyl ethyl ketone is Fisher Certified grade. Methanol is Fisher Optima grade. The explosives are used as received from the FAA. Gas chromatography with an electron capture detector (GC-ECD) and gas chromatography with a mass spectrometer detector (GC-MS) analysis did not reveal any significant impurities in the explosives.

EXPLOSIVE STANDARDS

Standards are prepared from dilutions of stock solution of a few mg of pure explosive (TNT, RDX or PETN) to 1 ml of methyl ethyl ketone. This stock solution is kept in an amber vial with a teflon lined cap and stored in a refrigerator to reduce sample degradation. Serial dilutions from the stock are made using methanol. These dilutions are prepared in amber vials with teflon lined crimp tops. To reduce loss of explosive molecules to the walls of the vials, dilutions are prepared six times in the same vial and discarded. The seventh dilution becomes the standard. These standards are also kept refrigerated. The dilution standards are only valid for 24 hours.

ION MOBILITY SPECTROMETER

IMS operating conditions. The IMS used in this study is a PCP model 110. In the IMS vaporized molecules are carried into a Ni-63 source where they are ionized and injected as a pulse (500 μ s wide in this study) into a drift region. Ions are separated in space within the drift tube, due to charge, mass and size differences. A typical spectra generated by the IMS for TNT, RDX and PETN with NO_2 as the reagent gas is shown in Figure 2. An IMS spectrum is a plot of voltage vs time. The voltage is related to the ion current arriving at the electrometer plate at the end of the drift tube and thereby to the quantity of explosive molecules entering the source.

To enhance the selectivity of the IMS for the detection of explosives the ion source can be seeded with molecules that either form adducts with the target analyte or reduce the background noise from interferents in the room air. In this study the ion source is seeded with methylene chloride (CH_2Cl_2) for TNT and RDX detection and nitrogen dioxide (NO_2) for PETN detection. These reagent gases are added using permeation tubes (VCI Metronics Inc.). The typical

concentration of the seed compound is 2.6 ± 0.6 ppm for the CH_2Cl_2 and 1.3 ± 0.3 ppm for NO_2 (based on a temperature of 20°C and a carrier gas flow of 250 ccm). The analyte ions detected under the above conditions were TNT-H^+ , $\text{RDX}\cdot\text{Cl}^-$ and $\text{PETN}\cdot\text{NO}_3^-$. A general review of IMS and the ion molecule chemistry of the Ni-63 source can be found in Plasma Chromatography⁸ and a recent review by St. Louis et al⁹.

Purified room air or bottled ultra high purity air is used as the carrier and drift gas in the IMS. A water bubbler is used in the carrier manifold in all of the experiments to add water vapor to the carrier gas¹⁰. This approach results in shorter instrument clearance times for the explosives and therefore increased sensitivities. The concentration of water is approximately 6 ppt. (based on the saturated vapor pressure of water in air at 20°C and a carrier gas flow rate of 250 ccm).

Calibration. Calibration data relating IMS response to the mass of explosives is generated by loading measured quantities of explosive onto the quartz wool plug in a preconcentrator. A typical calibration contains 30 points, 5 at each of 6 quantities (1000, 500, 100, 25, 5 and 0 pg). To reduce the variability in sample preparation, a modified Hewlett Packard autosampler (HP model 7673) is used to load the explosives onto the wool. Each injection is $2.5\ \mu\text{l}$ in volume. After allowing the solvent to evaporate (5 minutes) the preconcentrator is inserted into the inlet of the IMS. An external heater which is held at 100°C is then slid over the preconcentrator. The heater supplies a flow of heated purified air at a flow rate typically 50 ccm greater than the flow rate at which the IMS is drawing air through the preconcentrator. The heated air desorbs the explosives from the preconcentrator and carries the vapors into the IMS. The method of quantification of the explosives is outlined in Figure 3.

The output voltage of the IMS is monitored in a time window (typically $550\ \mu\text{s}$ wide) centered on the peak associated with the explosive to be quantified. The voltage in this window is integrated using a boxcar integrator (PCP model BC-10) and then subtracted from the integrated voltage in a background window. A new IMS scan is acquired every 26 msec (gate rep rate of 39 Hz). The signal - background voltage is next sent to an HP model 7673 series II integrator. The 7673 integrates the output voltage vs time. This final step is also performed using a software package called "Chrom-Perfect" by Justice Innovations. The software allows storage and post analysis inspection and manipulation of the data.

Vapor Generator Calibration

The vapor generator calibration procedure involves three steps, first the calibration of the IMS [precalibration] then the vapor generator and finally a second IMS calibration [post-calibration]. This process takes approximately 12 to 15 hours. The IMS calibration is repeated to assure that no significant drift in IMS response has occurred during the vapor generator calibration. The points from both IMS calibrations are combined to calculate the IMS response vs explosive

mass equation. This equation is then used to estimate the vapor generator mass output. A typical vapor generator calibration is performed at a set coil temperature and pulse width (5 seconds in this study) with the mass output varied by changing the carrier gas flow rate. The output could also be changed by varying the pulse width or both the carrier flow rate and pulse width. Varying the coil temperature to adjust the vapor generator mass output is not feasible in the IV&V tests due to the long equilibration time needed to reach the steady state saturated vapor concentration for the explosive in the coil.

Explosive vapors from the generator are collected using the quartz preconcentrators. The preconcentrator is positioned at the exit of the generator. A teflon washer is placed between the preconcentrator and the generator to assure that all of the vapors enter the preconcentrator. The typical DACS sampling method included a 5 sec presampling time followed by a 5 sec sample pulse and a 2 sec post sampling time. After the 12 seconds the preconcentrator is removed from the vapor generator outlet and placed immediately into the IMS inlet where a heater is slid over the preconcentrator to desorb the explosives into the IMS. Quantification of the sample is accomplished by integration of the IMS response as described in the IMS calibration section.

RESULTS AND DISCUSSION

ION MOBILITY SPECTROMETER CALIBRATION

The IMS calibrations (combined points from the pre and post-calibrations) for TNT, RDX, and PETN are shown in Figures 4, 5 and 6 respectively. The sensitivity of the IMS for TNT and RDX is similar, with both explosive calibration curves having slopes of approximately 0.02 (IMS response $\times 10^6$ / pg explosive, 0.023 for TNT and 0.020 for RDX). The intercept for the combined TNT calibrations is 119,000 while the intercept for RDX averaged 296,000. The IMS response for PETN was significantly less with a slope of 0.0065 and an average intercept of 5,000. Linear regression analysis of the IMS calibrations typically had R^2 values of >0.99 . Blanks were not included in the calculation of the calibration curves. The blanks did yield a measurable response however, therefore they dictate the baseline above which the IMS lower limit of detection for each explosive is calculated. The average response of the IMS for blanks is equivalent to 5 - 10 pg for TNT or RDX and 10 - 20 pg for PETN. The above quantities were estimated from the IMS calibration curves. Since preconcentrators are randomly selected during the calibration process, typically from a set of 5, preconcentrators used in the blank injections were used previously in an explosive injection. A possible scenario for the origin of the blank signal may be the following. Explosives are taken up in the methanol then redeposited at sites that are more thermally labile. Explosive molecules may also be released from the IMS inlet/source region if residual methanol exists on the preconcentrator quartz wool.

VAPOR GENERATOR CALIBRATION

As was mentioned in the experimental section the explosive output from the generator is monitored indirectly using the differential pressure change vs time (dPt) across the generator during a pulse. At this time the output volume is estimated using the product of nominal flow and pulse width. We are currently deriving the relationship between dPt and output volume. The curves resulting from the regression analysis of dPt vs nominal flow for the TNT, RDX, and PETN vapor generators are presented in Figure 7. A linear relation existed between dPt and flow rate for all of the vapor generators tested (typical $R^2 \geq 0.996$). Significant differences exist, however, between the slopes of the curves between vapor generators. The variation in the slopes could be the result of differences in resistance between the three coils, due to physical construction, changing resistance of the air with temperature (higher resistance at higher temperatures) and variations in the setup from day to day of the VG (i.e., flow rate resistance of the setup side of the vapor generator).

The IMS response vs dPt at a specific vapor generator coil temperature for each explosive are plotted in Figures 8 through 12. The mass output from the explosive vapor generators at the average dPt values associated with each of the nominal flow rates used in the calibrations (20, 40, 60, 80 and 100 ccm) are presented in Table I.

TABLE I

Calculated Vapor Generator Output in Picograms vs dPt, 5 Second Pulse, Preconcentrator Injection.

TNT, 18°C Coil Temperature:

dPt	Picograms	Standard Deviation	% Error (2σ)
1.26	55.4	19.9	72
2.34	103	19.5	38
3.51	155	19.5	25
4.42	196	19.6	20
5.97	264	20.4	15

TNT, 22°C Coil Temperature:

dPt	Picograms	Standard Deviation	% Error (2σ)
1.25	83.7	22.7	54
2.49	171	22.3	26
3.74	258	22.3	17
5.00	346	22.7	13
6.53	453	23.7	10

TABLE I, cont.

RDX, 61.9°C Coil Temperature			
dPt	Picograms	Standard Deviation	% Error (2σ)
1.93	112	20.7	37
3.79	222	21.8	20
5.68	333	24.1	14
7.60	446	27.5	12
9.61	564	31.8	11
RDX, 75.8°C Coil Temperature			
Dpt	Picograms	Standard Deviation	% Error (2σ)
1.99	557	187	67
3.79	850	185	44
5.77	1170	187	32
8.01	1540	194	25
10.1	1870	203	22
PETN, 64.4°C Coil Temperature			
dPt	Picograms	Standard Deviation	% Error (2σ)
2.55	340	164	96
4.76	571	161	56
7.01	807	159	39
9.44	1060	161	30
12.1	1340	165	25

The largest uncertainty in the vapor generator calibration is associated with the sample collection method. This point is illustrated by comparing the calibration for the PETN generator done using preconcentrators (Figure 12 and Table I) with the calibration done using direct transfer of the explosive vapors into the IMS through a heated quartz lined transfer tube (Figure 13 and Table II). The direct transfer calibration was done within two hours of the preconcentrator calibration with the PETN vapor generator's coil at the same temperature. A significant decrease in the standard deviation is observed, from 160 to 26. The direct transfer method was tried for the other 2 generators with similar improvement in the precision of the calibrations. While it reduces the variability in response the direct transfer method can not be used at this time because the temporal profile of the injection of the explosives is significantly shortened and not representative of a calibration injection. Figure 14 shows a comparison of the temporal IMS response for the two types of injection methods (preconcentrator and direct injection) along with an injection of 1,000 pg of PETN from a standard. The resulting increased concentration of explosives in the IMS source with the direct transfer method is out of the linear response region of the IMS and therefore results in a decreased sensitivity. This decreased sensitivity is indicated by the lower mass quantities observed in the direct transfer

vapor generator calibration vs the preconcentrator method (ie 1,060 vs 1340 pg PETN output at 64.4 °C coil temperature, 100 ccm flow rate and a 5 second pulse width). This phenomena of an apparent reduction in the vapor generator output was also observed in the other 2 generators when calibrated using the direct transfer line.

Table II

Calculated Vapor Generator Output in Picograms vs dPt, 5 second Pulse, Direct Injection, PETN

dPt	Picograms	Standard Deviation	% Error (2σ)
2.47	309	26.4	17
4.77	490	26.0	11
7.06	670	26.1	8
9.52	864	26.8	6
12.0	1060	28.1	5

A comparison of the measured mass output from all 3 of the generators with the estimated mass output is reported in Table III. The mass output from the generators is calculated using the following equilibrium vapor pressure equations reported by Dionne et al¹¹ with the resulting vapor pressure incorporated in Equation 4.

$$(1) \quad TNT, \quad \text{Log } P_{(ppb)} = \frac{-5481}{T(K)} + 19.37$$

$$(2) \quad RDX, \quad \text{Log } P_{(ppT)} = \frac{-6473}{T(K)} + 22.50$$

$$(3) \quad PETN, \quad \text{Log } P_{(ppT)} = \frac{-7243}{T(K)} + 25.56$$

$$(4) \quad pg_{(output)} = 2.03 \times 10^{-4} K \min ml^{-1} mole^{-1} sec^{-1} (flow, ml \min^{-1}) (pulse, sec) (P_{(ppT)}) (mw, g mole^{-1}) (T_{(amb)}^{-1})$$

flow = flow rate of the carrier gas

pulse = width of explosive vapor pulse

$P_{(ppT)}$ = equilibrium vapor pressure of explosive, parts per trillion

mw = molecular weight of explosive

$T_{(amb)}$ = ambient temperature

TABLE III

Comparison of Predicted vs Observed Vapor Generator Mass Output in Picograms. Vapor Generator condition, 5 second Pulse, 20 and 100 ccm Flow Rates.

Explosive	VG Temp., °C	Predicted	Observed
TNT	18	54-270	52-257
TNT	22	97-486	80-445
RDX	61.9	23-114	109-561
RDX	75.8	135-673	531-1865
PETN	64.4	271-1356	326-1323

Referring to Table III, the observed output of the TNT and PETN generators were within $\pm 20\%$ of the expected value. The RDX generator output, however, was up to 393% greater than expected. The reason for this discrepancy may be due to the RDX coil design (see experimental). The last foot of tubing was maintained at 5°C above the coil temperature to reduce the loss of explosives to the tubing walls. One scenario for the elevated mass output is the presence of solid explosive in this last foot. This would result in the generator output being a sum of two sources of RDX vapors. A temperature rise of 5°C above the coil temperature of 61.9°C would increase the mass output at 100 ccm with a 5 sec pulse width from 114 pg to 193 pg. Clearly some other mechanism is causing this anomaly.

A graphical comparison of the vapor pressure of TNT, RDX and PETN as reported by a number of investigators is shown in Figures 15 through 17. These graphs were copied from an article by Dionne et al¹⁰. The vapor pressure of the explosives in this study estimated from the mass output from the generator are included in the above graphs. The graphs show that even the RDX data from this study is consistent with that previously reported.

Conclusions

Preliminary calibrations have been performed for all three vapor generators (TNT, RDX, and PETN) using the IMS. Linear regression analysis for the vapor generators typically resulted in $R^2 > 0.85$. The generators are calibrated in the following ranges: TNT, 52 to 445 pg; RDX, 109 to 1,000 pg; and PETN, 326 to 1000 pg. The calibrations have shown that the vapor generators are capable of delivering a mass of explosives very close to that predicted from vapor pressure calculations. What remains to be done is to repeat the calibrations

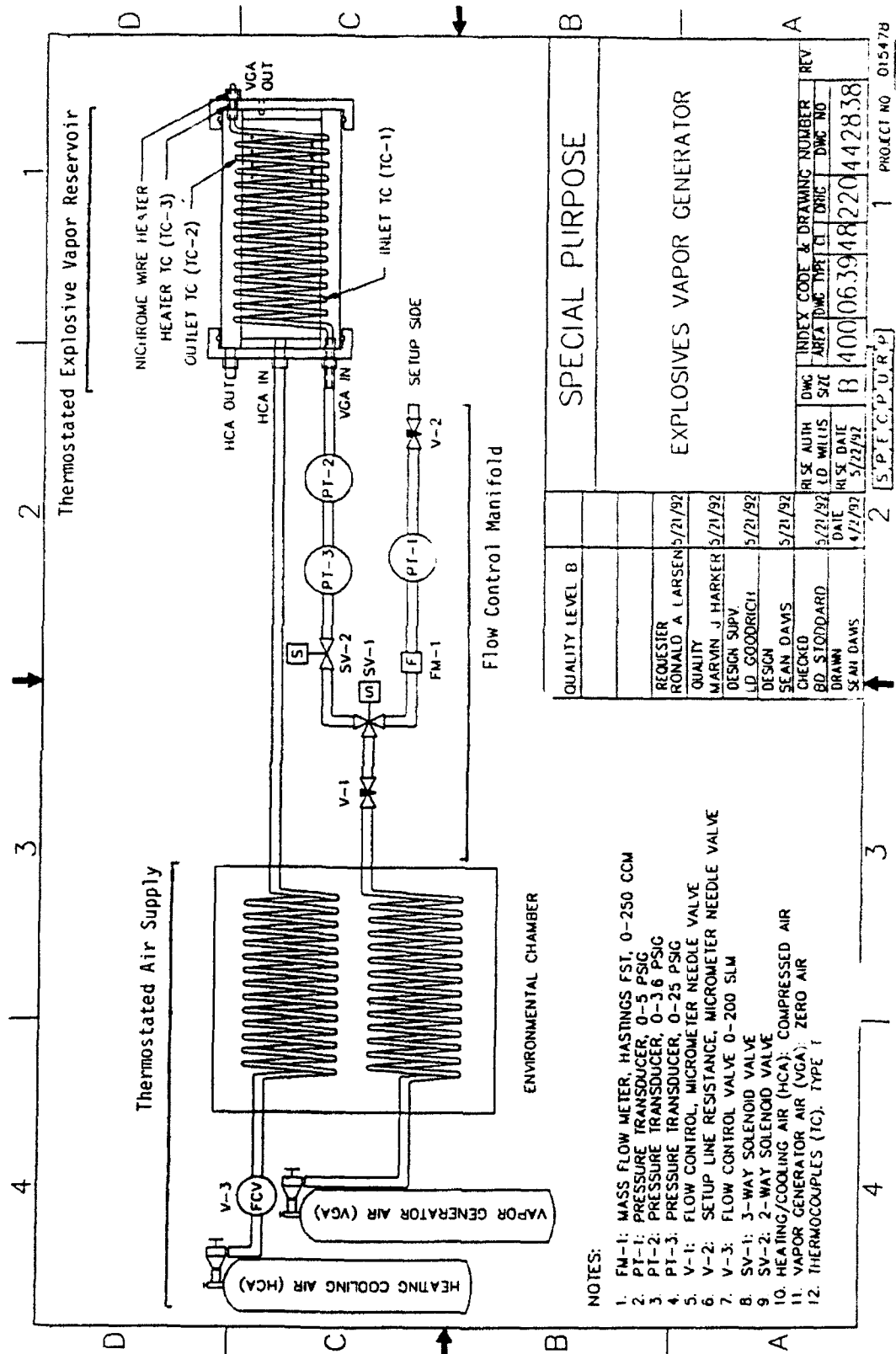
with the aim of lowering the calibration to 1 pg and to verify that the generator can reproducibly emit a known quantity of explosives by control of flow, pulse width, and VG temperature.

Calibration of the vapor generator in the 1 pg limit will be possible only with an increase in the sensitivity of the calibration standard, the IMS. The lower limit of detection of the IMS in the case of preconcentrator injection is dictated by the chemical noise associated with the preconcentrator. Therefore the preconcentrator introduction method should be replaced in both the IMS and the vapor generator calibrations with an introduction method of higher precision and one that results in a higher sensitivity. A possible alternative would be a GC introduction system. GC-IMS systems have been reported to have sensitivities in the sub-picogram (900 femtograms) range for TNT.

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Figure 1. Explosive Vapor Generator



IMS Spectrum from 50 picograms TNT, 50 picograms RDX, and 75 picograms PETN

GAL Monitor 17:06:04 13/11/91 Loading From C:\ASP\DATA\EGG15856.A
Comment - #158, EG8G, 160C, 100x500 Tank Air, Bbblr &NO2, Gain 2

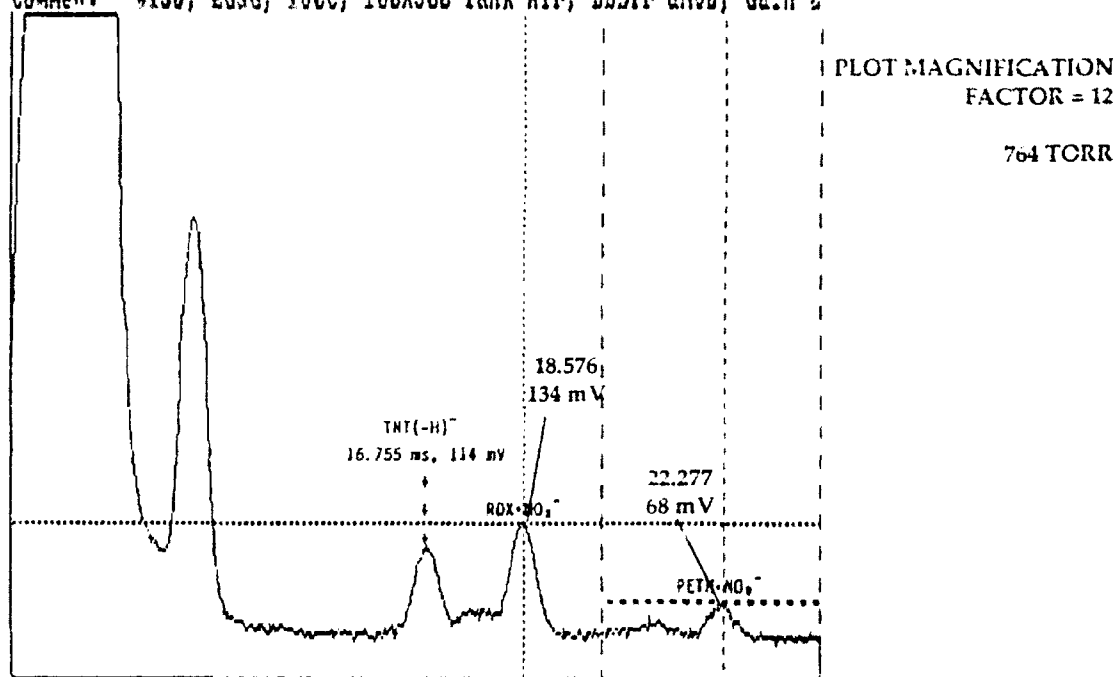


FIGURE 2.

EXPLOSIVE VAPOR GENERATOR CALIBRATION FLOW DIAGRAM

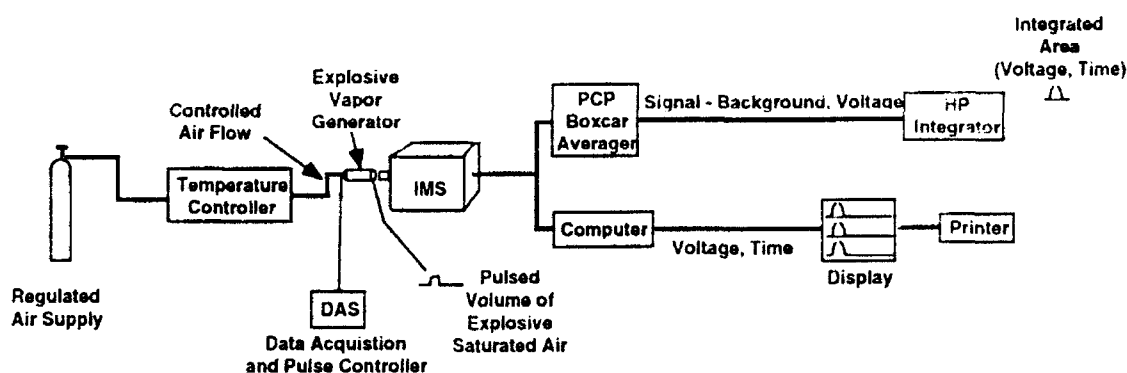


FIGURE 3.

TNT Combined 1st and 2nd IMS Calibration

Regression Equation (WLS):

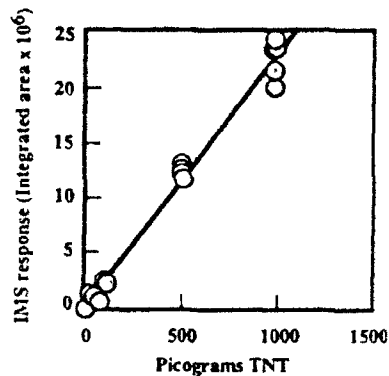
$$\text{IMS response} = .119 + (.0231)(\text{picograms TNT})$$

Inverse Equation:

$$\text{Picograms TNT} = -5.15 + (43.3)(\text{IMS response})$$

$$R^2 = .994$$

$$N = 50$$



Picograms TNT	Repeatability C.V. (%)	95% Prediction Interval (± picograms)
5	26	5 ± 8.5
25	16	25 ± 18
100	2.8	100 ± 37
500	3.6	500 ± 83
1000	5.5	1000 ± 119

FIGURE 4.

RDX COMBINED 1ST AND 2ND IMS CALIBRATION

Regression Equation (WLS):

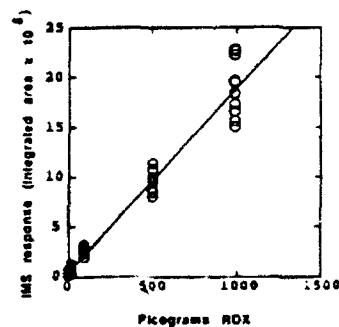
$$\text{IMS response} = 0.296 + (.0199)(\text{picograms RDX})$$

Inverse Equation:

$$\text{Picograms RDX} = -1.48 + (50.3)(\text{IMS response})$$

$$R^2 = .965$$

$$N = 50$$



Picograms RDX	Repeatability C.V. (%)	95% Prediction Interval (± picograms)
5	44	5 ± 14
25	33	25 ± 22
100	13	100 ± 54
500	12	500 ± 229
1000	15	1000 ± 449

FIGURE 5.

PETN COMBINED 1ST AND 2ND IMS CALIBRATION

Regression Equation (WLS):

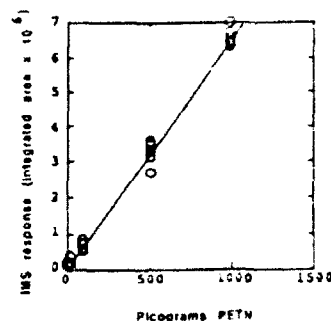
$$\text{IMS Response} = .00494 + (.00652)(\text{picograms PETN})$$

Inverse Equation:

$$\text{Picograms PETN} = -.757 + (153.3)(\text{IMS response})$$

$$R^2 = .995$$

$$N = 43$$



Picograms RDX	Repeatability C.V. (%)	95% Prediction Interval (± picograms)
5	75	5 ± 36
25	66	25 ± 37
100	16	100 ± 41
500	7.9	500 ± 57
1000	3.1	1000 ± 75

FIGURE 6.

REGRESSION ANALYSIS OF NOMINAL FLOW VS INTEGRATED FLOW VAPOR GENERATOR CALIBRATION RUNS

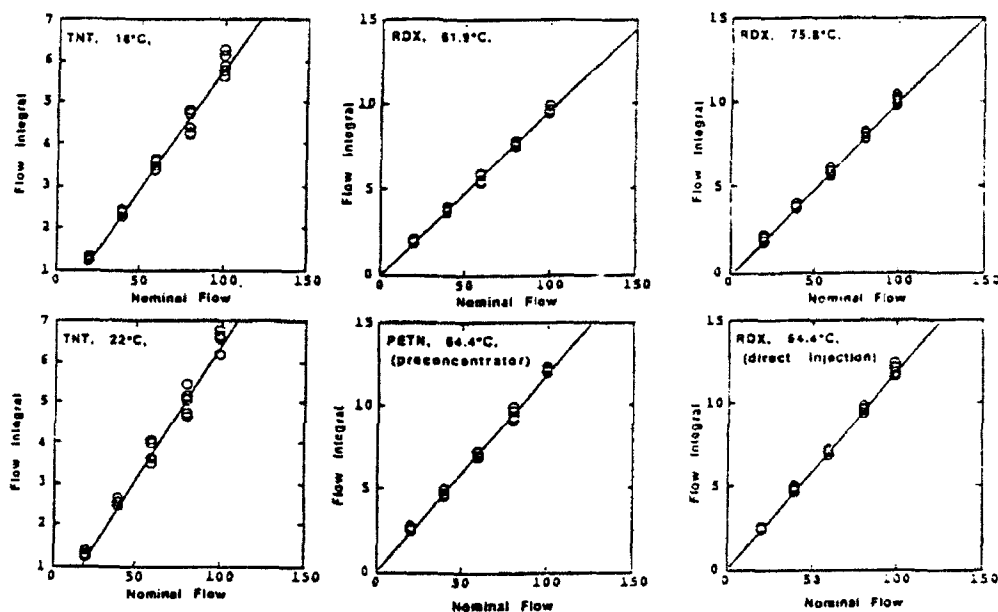


FIGURE 7.

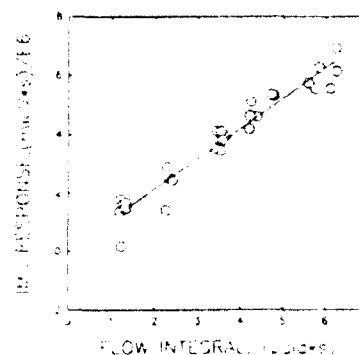
TNT VAPOR GENERATOR CALIBRATION PRECONCENTRATOR INJECTION, 5 SEC PULSE, 18 C

Regression

Equation: $\text{IMS Response} = 0.107 + 1.027 * (\text{VGFI})$

$R^2 = 0.940$

$N = 30$



Vapor Generator Flow	Average Flow Integral	95% Prediction Interval (IMS area \pm uncertainty)
20	1.26	1.40 (0.94)
40	2.34	2.51 (0.92)
60	3.51	3.71 (0.92)
80	4.42	4.65 (0.92)
100	5.97	6.24 (0.95)

FIGURE 8.

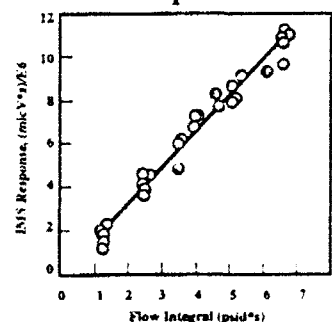
TNT Vapor Generator Calibration, Preconcentrator Injection 5 second pulse

Regression Equation:

$\text{IMS response} = 0.031 + 1.620 * (\text{VGFI})$

$R^2 = 0.975$

$N = 30$

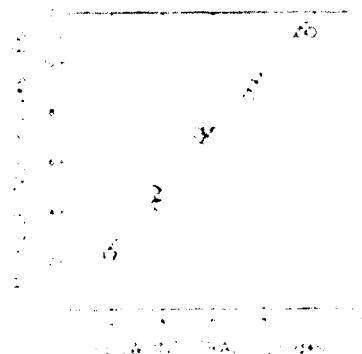


Vapor Generator Flow	Average Flow Integral	95% Prediction Interval (IMS area \pm uncertainty)
20	1.25	2.06 (1.08)
40	2.49	4.07 (1.05)
60	3.74	6.09 (1.04)
80	5.00	8.13 (1.05)
100	6.53	10.61 (1.08)

FIGURE 9.

RDX VAPOR GENERATOR CALIBRATION, PRECONCENTRATOR INJECTION, 5 SEC PULSE, 61.9 C

Regression Equation:
 IMS Response = $0.265 + 1.171 \cdot (\text{VGFI})$
 $R^2 = 0.985$
 N = 25(4 outliers eliminated from analysis)

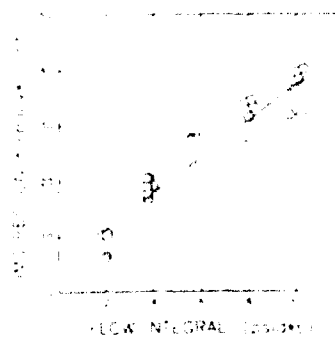


Vapor Generator Flow	Average Flow Integral	95% Prediction Interval (IMS area \pm uncertainty)
20	1.93	2.52 (0.83)
40	3.79	4.70 (0.81)
60	5.68	6.91 (0.81)
80	7.60	9.16 (0.82)
100	9.61	11.52 (0.86)

FIGURE 10.

RDX VAPOR GENERATOR CALIBRATION PRECONCENTRATOR INJECTION, 5 SEC PULSE, 75.8 C

Regression Equation:
 IMS response = $4.970 + 3.239 \cdot (\text{VGFI})$
 $R^2 = 0.883$
 N = 30

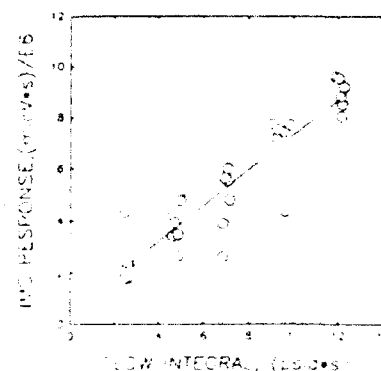


Vapor Generator Flow	Average Flow Integral	95% Prediction Interval (IMS area \pm uncertainty)
20	1.99	11.36 (7.56)
40	3.79	17.20 (7.41)
60	5.77	23.81 (7.34)
80	8.01	30.86 (7.40)
100	10.06	37.50 (7.58)

FIGURE 11.

PETN VAPOR GENERATOR CALIBRATION PRECONCENTRATOR INJECTION, 64.4 C

Regression Equation:
IMS Response = $0.480 + 0.683 \cdot (\text{VGFI})$
 $R^2 = 0.845$
 $N = 30$

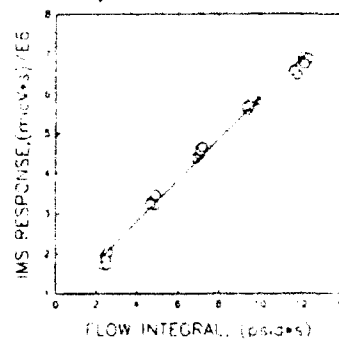


Vapor Generator Flow	Average Flow Integral	95% Prediction Interval (IMS area \pm uncertainty)
20	2.55	2.22 (2.19)
40	4.76	3.73 (2.14)
60	7.01	5.27 (2.13)
80	9.44	6.93 (2.14)
100	12.11	8.76 (2.20)

FIGURE 12.

PETN VAPOR GENERATOR CALIBRATION, DIRECT INJECTION, 5 SEC PULSE, 64.4 C

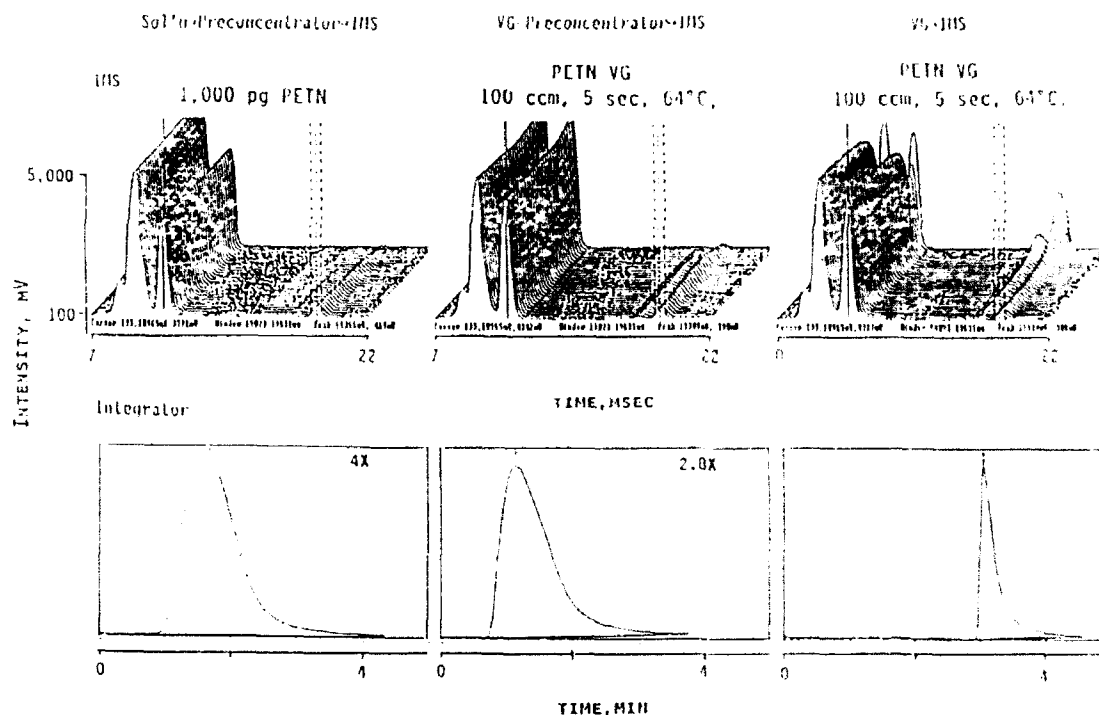
Regression Equation:
IMS Response = $0.753 + 0.513 \cdot (\text{VGFI})$
 $R^2 = 0.992$
 $N = 30$



Vapor Generator Flow	Average Flow Integral	95% Prediction Interval (IMS area \pm uncertainty)
20	2.47	2.02 (0.35)
40	4.77	3.20 (0.34)
60	7.06	4.38 (0.34)
80	9.52	5.64 (0.34)
100	12.00	6.91 (0.35)

FIGURE 13.

FIGURE 14. IMS Response vs Injection Methods



Vapor Pressure of TNT

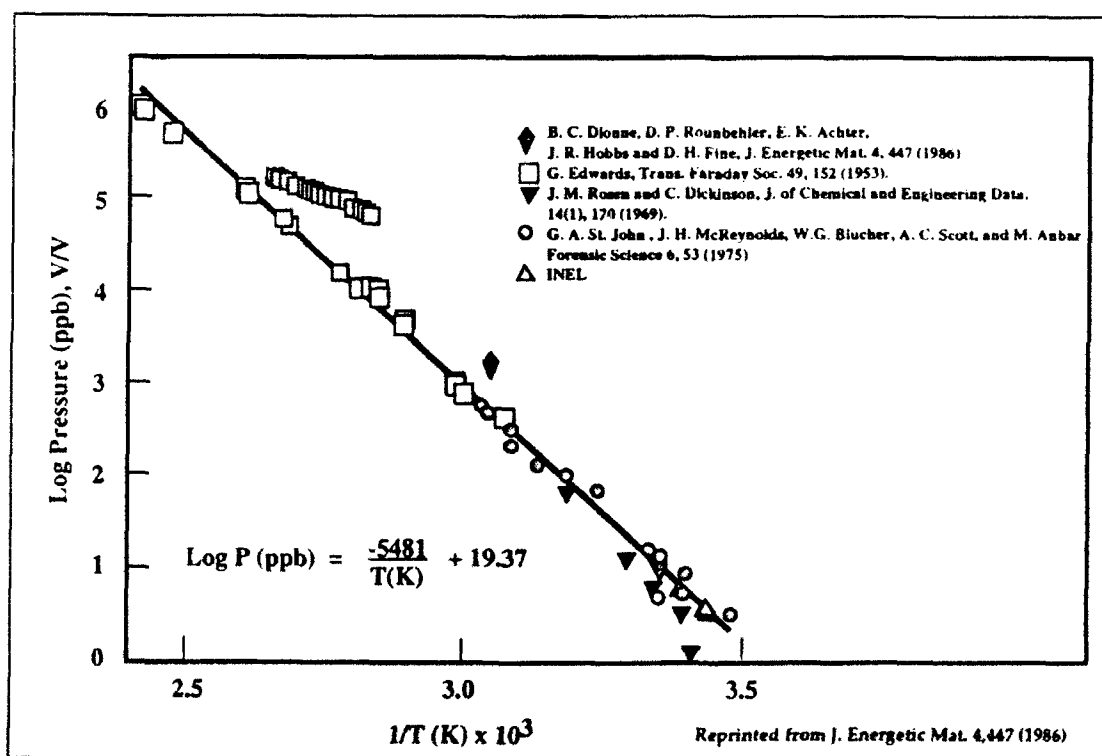


FIGURE 15.

Vapor Pressure of RDX

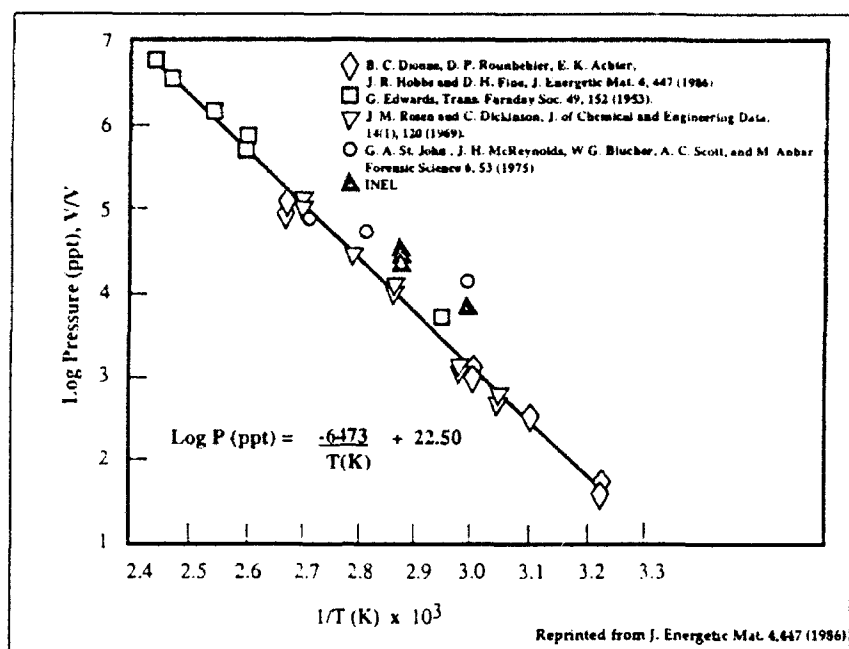


FIGURE 16.

Vapor Pressure of PETN

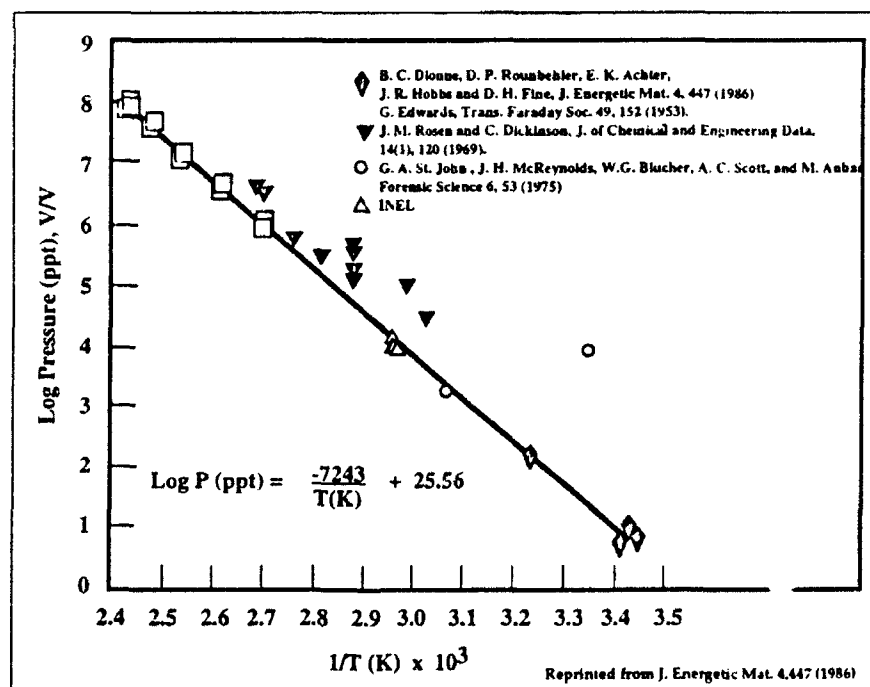


FIGURE 17.

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Advances in Analysis and Detection of Explosives

Proceedings of the 4th International Symposium on Analysis and Detection of Explosives, September 7-10, 1992, Jerusalem, Israel

Edited by
Jehuda Yinon

This volume includes the latest developments in the analysis and detection of explosives as presented at the 4th International Symposium on Analysis and Detection of Explosives held in Jerusalem, September, 1992.

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- explosive detection;
- vapor generators.

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